On-the-fly, off-lattice KMC simulations on experimental time scales with k-ART

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Molecular and Materials Modelling Summer School
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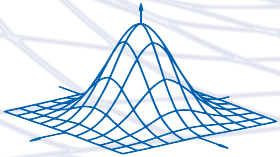
THE UNIVERSITY OF WARWICK



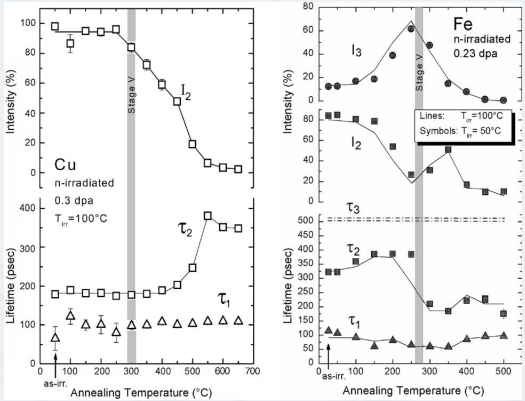
WCPM

Point defect complexes

Motivation

- Irradiation causes defect cascades.
- Leaves behind point defects:
  - self-interstitial atoms (SIA)
  - vacancies

  and complexes:
  - dislocation loops
  - stacking fault tetrahedra
  - nanovoids
  - ...



Eldrup and Singh, *J. Nucl. Mater.* **323**, 346 (2003)

- Wealth of defect clusters and events: impossible to predict.
- Time scale is beyond MD (milliseconds – hours).
- Complex energy landscape.

Outline

1. Kinetic Activation Relaxation Technique
   - Kinetic Monte Carlo
   - off-lattice
   - self-learning
   - handles small barriers
2. Applications
   - Vacancies in α-iron
   - Amorphous silicon
   - Annealing in ion-damaged silicon
   - Vacancies near Cu–Zr interface

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The kinetic Activation-Relaxation Technique

Kinetic Monte Carlo method

Execute events according to KMC rules.

off-lattice

- Not constrained to lattice (more systems).
- Account for long-range elastic effects.

self-learning

- ART nouveau (fast unbiased saddle point search) to generate events
  - on the fly
  - corrected for long-range effects.
- Store events: Build topology-based catalog.

El-Mellouhi, *PRB* **78**, 153202 (2008). Béland *PRE* **84**, 046704 (2011).

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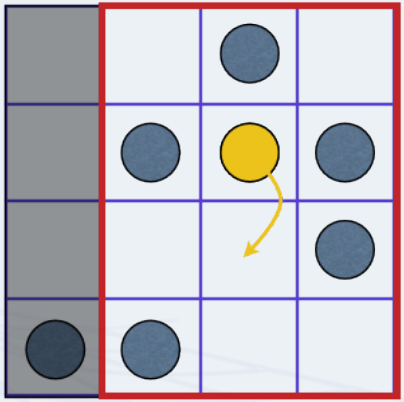
Standard KMC

- Problem must be lattice based.
- List of possible events is constructed
- Rate r_i from transition state theory: $r_i = r_0 \exp(-\Delta E / k_B T)$.
- One event picked at random.
- Clock advanced by $\Delta t = -\ln \mu / \sum_i r_i$, μ: Random number $\in (0; 1]$.



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

Limitations

- Predefined, limited catalogue of known events at $T = 0$.
- Ignores long-range interactions between defects.

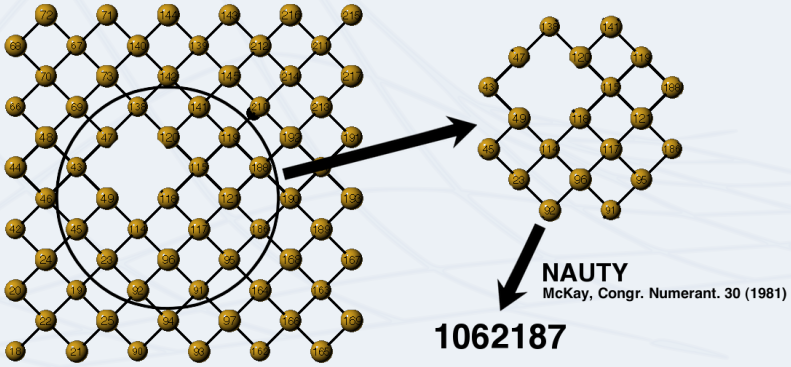
Topologies

Cluster centered on each atom

- Topological analysis: Which atoms are neighbours?
- Assign a key to each graph.

$\Rightarrow$ 1:1 relationship between keys and local structures.

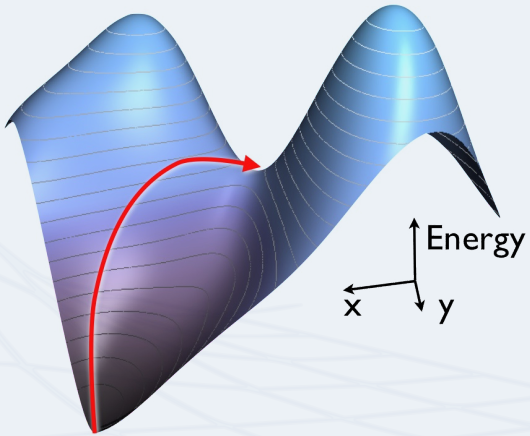
Search for events for each topology.



Find saddle points with ART nouveau

Activation-relaxation technique

1. Random displacement.
2. Leave harmonic well: negative eigenvalue.
3. Push up along corresponding eigendirection, minimize energy in perpendicular hyperplane.
4. Converge to saddle point.



5. Move configuration over the saddle point and relax to new minimum.

Barkema, Mousseau, PRL 77 (1996); Malek, Mousseau, PRE 62 (2000);

Events

Search for events

Find events centered on representative atom.

- Random displacement.
- Find saddle point (Lanczos, DIIS).

Expensive, but finds generic events for topology.

For lowest 99.99% of barrier weight:

Refine event for each specific atom.

- Few iterations to exact critical points.
- Takes into account specific local situation.

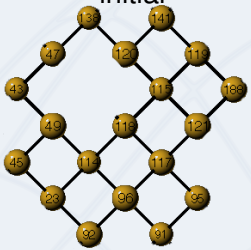
Tree of events

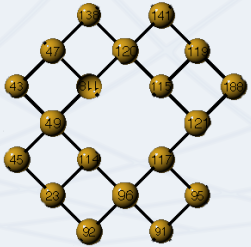
- Calculate rates $r_i = r_0 \exp(-\Delta E_i / k_B T)$, $r_0 = 10^{13}$ s^{-1}.
- Use tree to select event with proper probability.

Reconstructing events

Geometric transformation

Stored event
initial



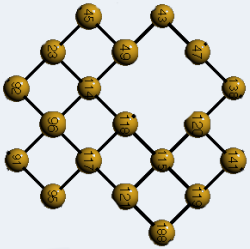


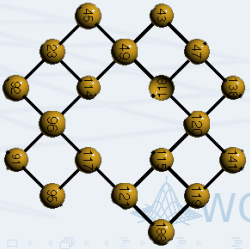
- Extract symmetry operation needed to transform stored event to configuration.

⇐ ⇒

- Apply same operation to final (saddle) state.

Configuration





Remembering events

Generic events

- Kept, even though the topology might disappear, but removed from tree.
- Topology reappears: Events reinserted to tree.
- Generic events can be imported from previous runs.

Atom keeps topology

Specific events:

- refined.

Atom changes topology

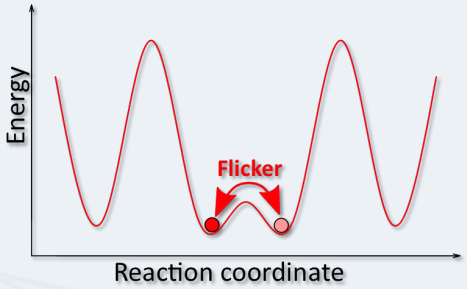
Specific events:

- Old ones removed.
- New ones calculated.

Béland, Brommer, *et al.*, *Phys. Rev. E* **84**, 046704 (2011).

Local configurations with low barriers

- k-ART might get trapped.
- Many events, no progress.



Requirements

- Correct distribution of exit states.
- Low overhead.

⇒ The basin auto-constructing Mean Rate Method
MRM: Puchala *et al.*, *J. Chem. Phys.* **132**, 134104 (2010)

The Mean Rate Method (MRM)

Transient states	$\Leftrightarrow$	Absorbing states
connected by low barriers.		connected to transient states by high barriers.

Basin exploration

- costly
- even unneccessary (early exit to absorbing state)

$\Rightarrow$ Explore/construct basins on the fly!

Relevant entities: events, not states

basin event	$\Leftrightarrow$	exit event
connects transient states.		connects transient state to absorbing state.

WCPM

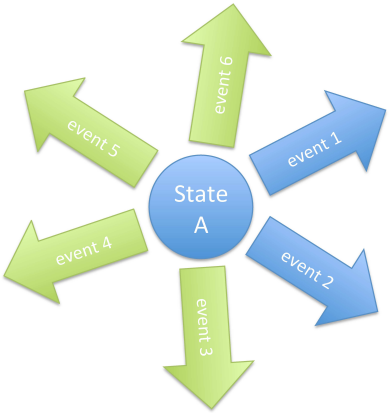
The Basin Mean Rate Method

Start from State A

- Identify events.
- If any event could be a basin event (judge by barrier):
  activate basin method.

Pick an event:

- Ordinary event: Go on normally
- Potential basin event: Start basin:
  - Execute event
  - Block event
  - Keep all other events.

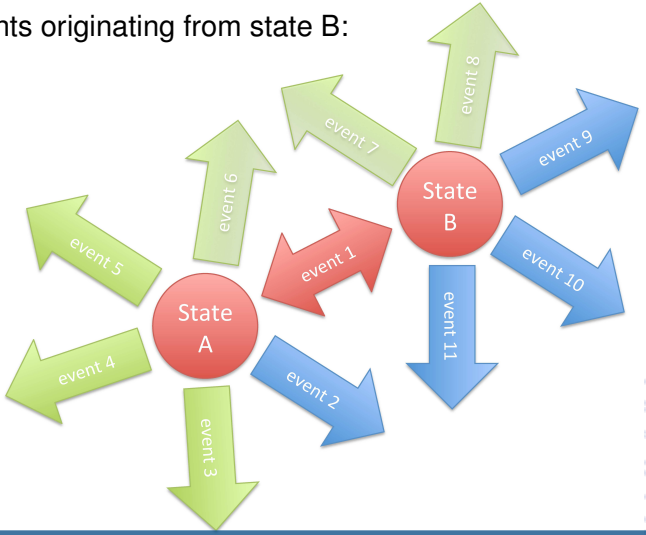


Legend

Green: Ordinary event
Blue: Potential basin event
Red: Basin event

In the basin

Search for new events originating from state B:



Legend

Green: Ordinary Blue: Potential basin Red: Basin

The basin auto-constructing Mean Rate Method

Features

- Basin is built on the fly.
  - Basin explored only as far as needed.
  - Integrates seamlessly into k-ART.
- No state is visited twice.
- Averages over “low” barriers.
- Correct distribution of absorbing states.
- However: Ignores correlation between basin residence time and absorbing state (short residence time: absorbing state closer to initial state).

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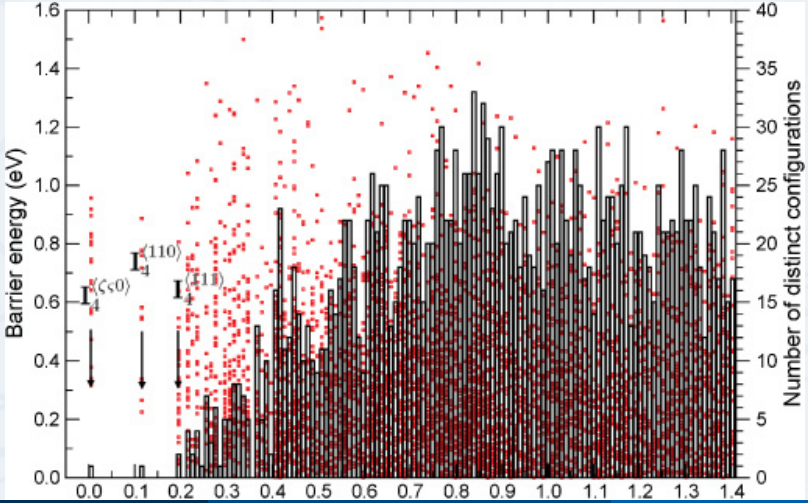
WCPM

Atomistic simulation of α-Fe: Challenges

Kinetic Monte Carlo simulations of α-Fe

Extremely rich in states and events:
e.g. 4-SIA cluster: more than 1500 distinct configurations.



Vacancies

Vacancy cluster agglomeration in bcc Fe

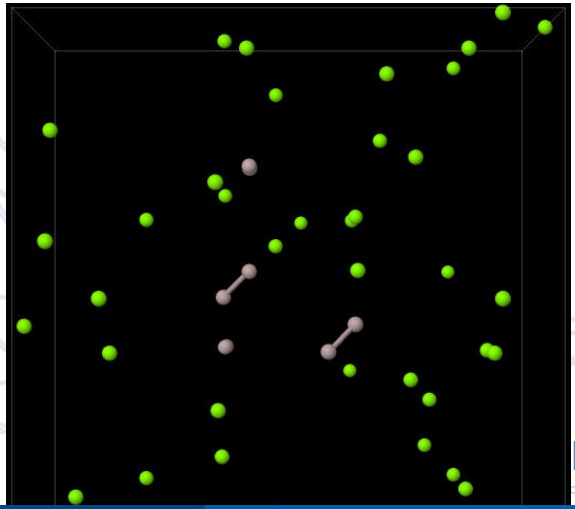
- Slower dynamics than interstitials.
- PAS results available.

The system: 2000 atoms

Remove atoms at random.

- Temperature 50°C.
- Display only vacancies, color code cluster size, green: monovacancies.
- Ackland-Mendelev potential (optimized).

Ackland *JP:CM* **16**, S2629 (2004)



50 vacancy k-ART simulations at 50 °C

Cluster growth

Average size > 6

- 0.1 ms

Time scale

Vacancy clustered:

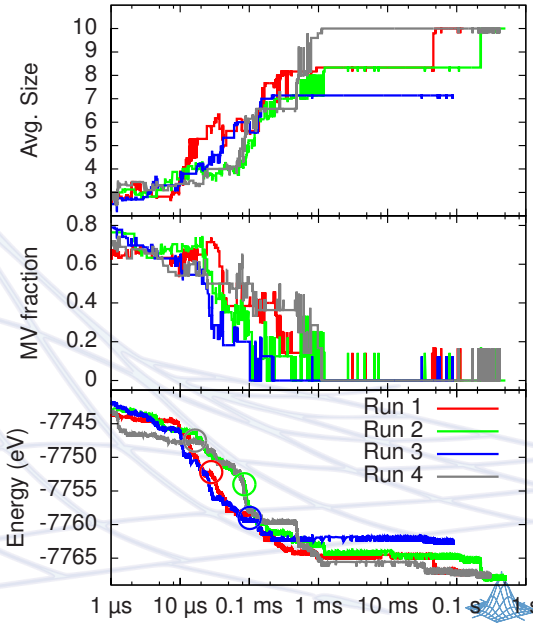
- 1 ms

Energy barriers

Maximal eff. barrier:

- 0.8–1.1 eV

Brommer & Mousseau, PRL **108**, 219601 (2012)



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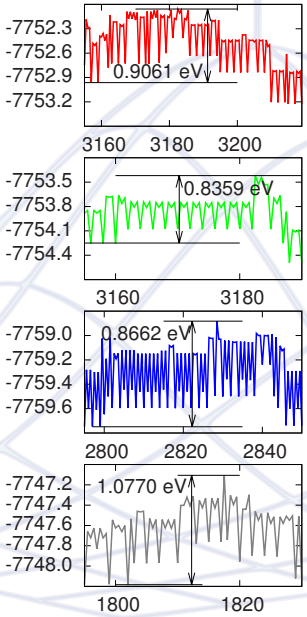
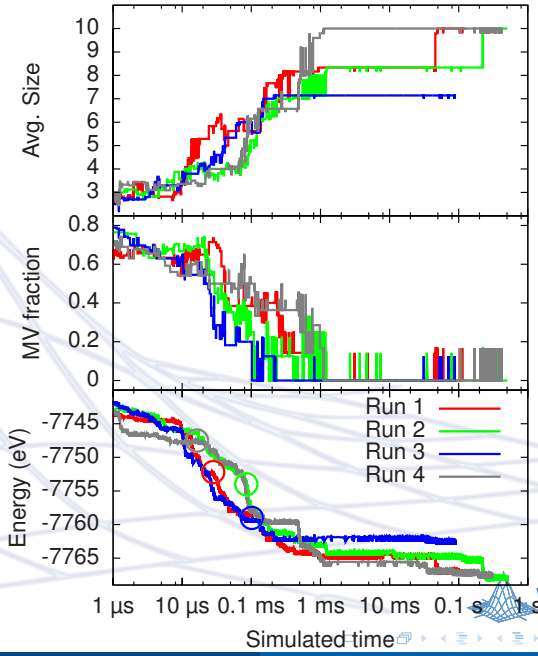
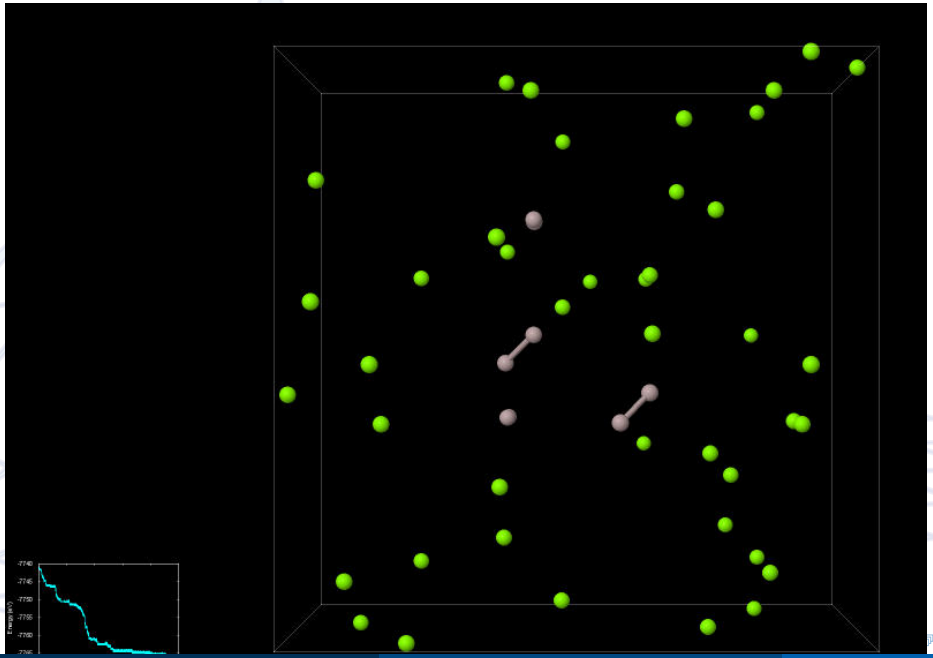
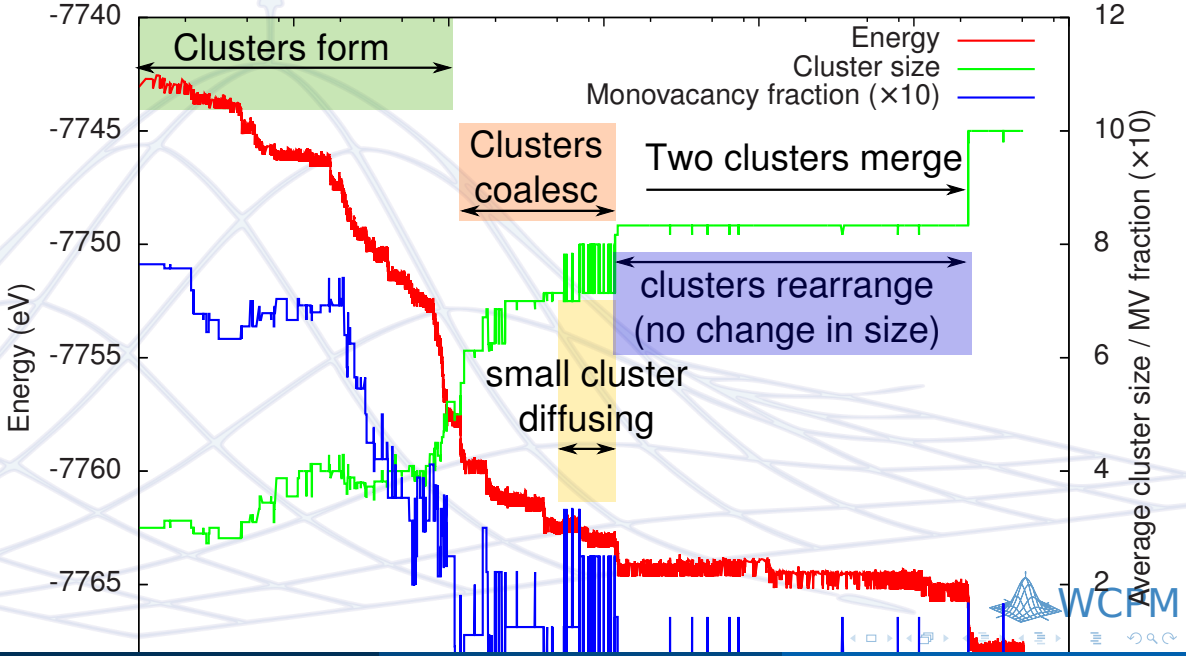




50 vacancies in α Fe



Trajectory in detail



Experimental results

Positron Annihilation Spectroscopy

Iron irradiated at 50°C:[a]

- Significant intensity from nanovoids as irradiated (nanovoids: clusters of 9–14 vacancies).
- Annealing over 150°C: Larger voids appear (40–50 V)

$\Rightarrow$ k-ART simulation agrees with experiment

[a] Eldrup and Singh, *J. Nucl. Mater.* **323**, 346–353, 2003.

Previous results: Autonomous Basin Climbing

- ABC[a] always picks lowest new barrier.
- k-ART may pick higher barrier, accounts for multiplicity.

Complete catalog essential for material description.

[a] Fan *et al.*, PRL **106**, 125501 (2011)

Energy release

More energy in cluster shape than cluster size

Typical cluster binding energy:

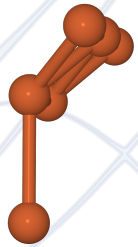
- 0.2 eV

also $\approx$ divacancy binding energy.

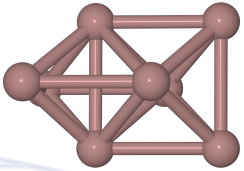
Reshaping a cluster:

- more than 1 eV

Example: di- & hexavacancy



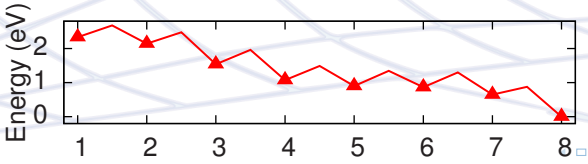
1



8

Initial

Final



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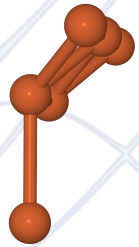
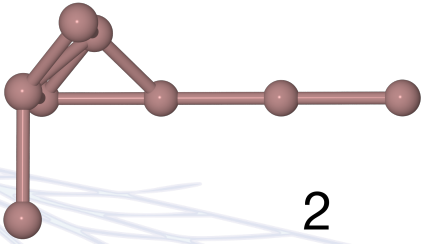
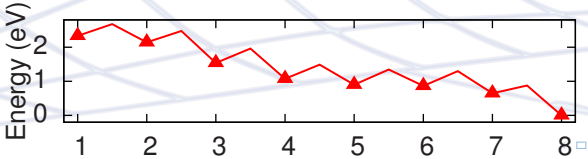


1



2

Simulated time: 4.54 µs — Barrier: 0.342 eV — ΔE: −0.191 eV



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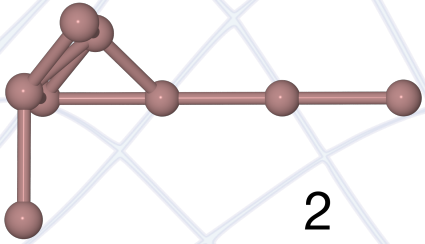

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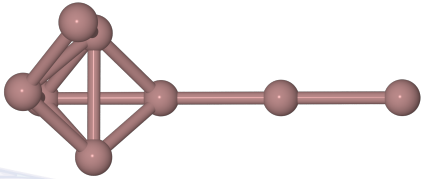
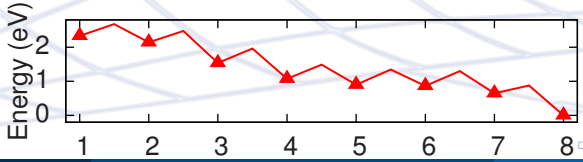


3

Simulated time: 4.62 µs — Barrier: 0.334 eV — ΔE: −0.603 eV



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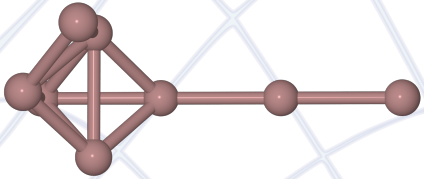

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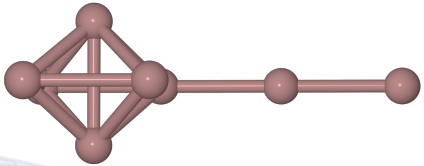
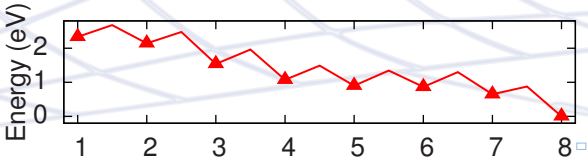


4

Simulated time: 5.61 µs — Barrier: 0.421 eV — ΔE: $-$0.464 eV



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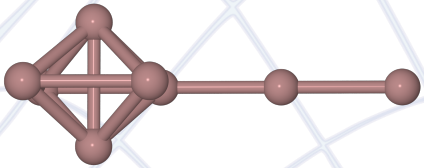

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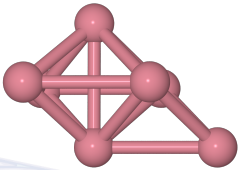
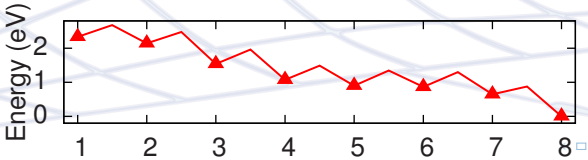


5

Simulated time: 6.14 µs — Barrier: 0.414 eV — ΔE: −0.177 eV



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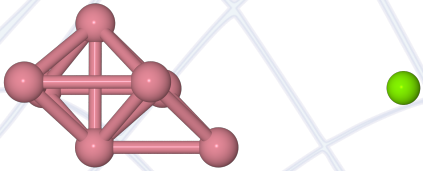

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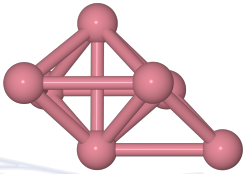
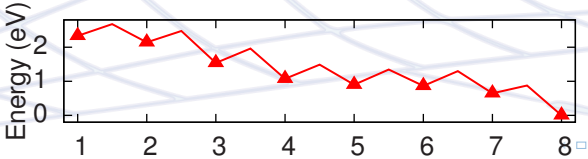


6

Simulated time: 6.26 µs — Barrier: 0.445 eV — ΔE: $-$0.033 eV



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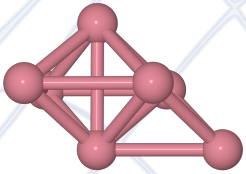

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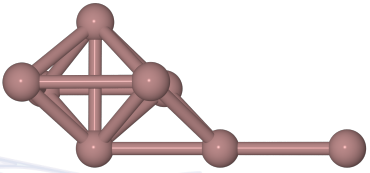
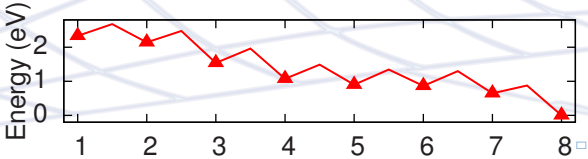


7

Simulated time: 7.11 µs — Barrier: 0.434 eV — ΔE: $-$0.216 eV



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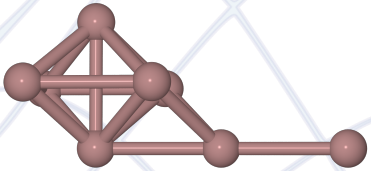
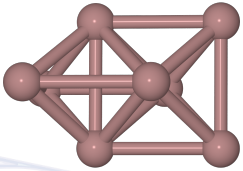
- more than 1 eV

Example: di- & hexavacancy

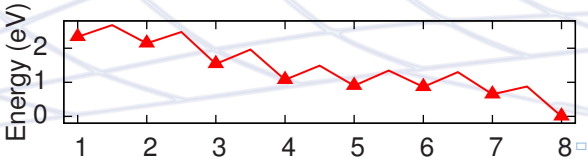


7

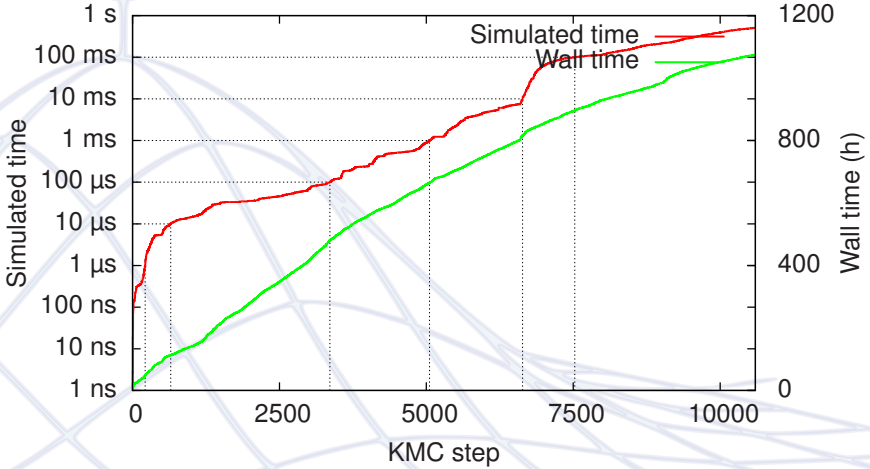


8

Simulated time: 17.19 µs — Barrier: 0.228 eV — ΔE: −0.649 eV



Accelerating simulation



Reasons

1. Lower effective energy barriers die out.
2. Basin acceleration threshold increased.

Increasing basin threshold

Optimal basin threshold

There is an optimal value for the basin threshold:

Too low: No progress.

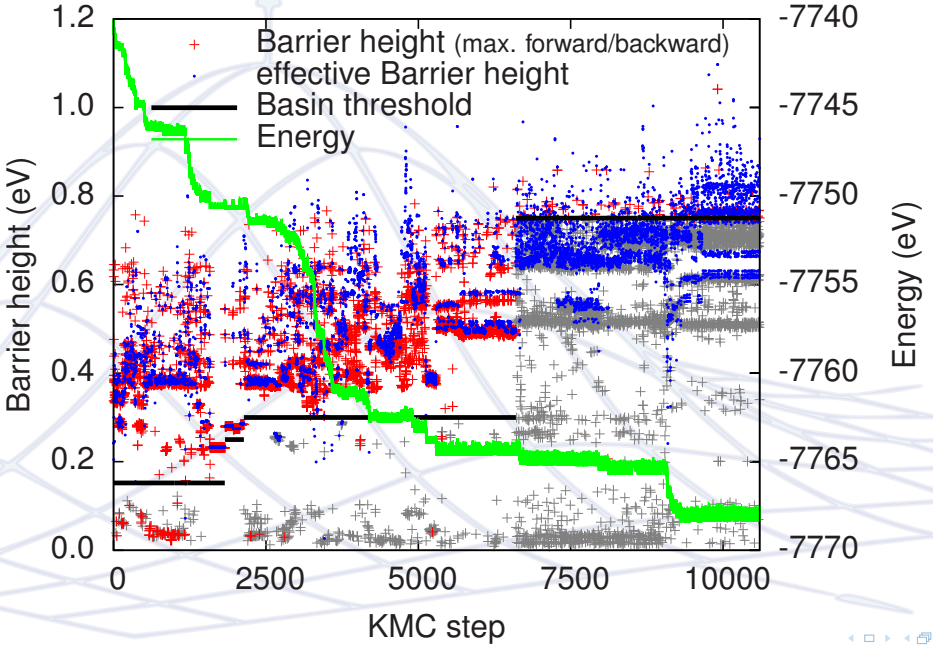
Too high: Too many states in basin:

- Lose trajectory
- Memory requirements.

Gradual increase during simulation.

WCPM

Basin Threshold



Conclusions: α-iron

Vacancies in bcc iron

- Vacancies cluster in nanovoids on a sub-second timescale.
- Full event catalog essential.
- Efficiently accelerated by bac-MRM.Brommer *et al.*, Phys. Rev. B **90**, 134109 (2014)

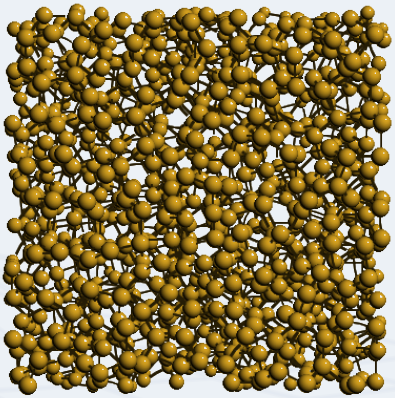
Amorphous silicon

Disordered metastable phase of Si

Defects in amorphous silicon:

- Are vacancies stable defects?
- Do vacancies diffuse?

No accelerated technique has been applied to disordered materials.



Project of Jean-François Joly (Ph.D. student UdeM, then Post-Doc Ottawa/Carleton).

WCPM

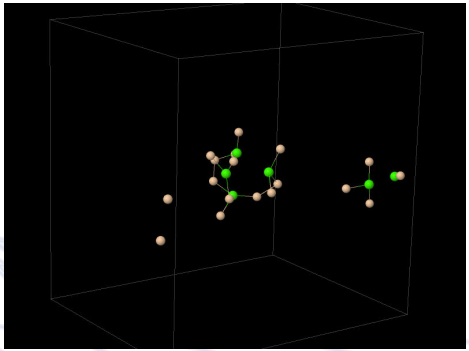
k-ART simulation of a vacancy in a-Si

The system

- 999 ($= 1000 - 1$) atoms.
- Mod. Stillinger-Weber potential.
- T $= 300$ K

Challenges

- Every atom: unique topology. Initial catalog: 32 120 events.
- Flickers on every energy scale.
  Basin threshold: 0.35 eV.

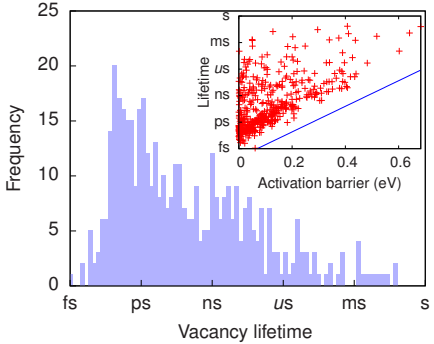


Results: Vacancies in a-Si

1000 k-ART runs

(one for each site as vacancy)

- Most times:
  Vacancy disappears
  - in initial minimization (547)
  - or first few steps (ns) (175).
- Survivors
  - 1 µs: 47
  - 1 ms: 13
  - at the end: 6 for 0.12–1.98 s.



Joly, PB, *et al.*, PRB **87**, 144204 (2013)

Vacancy diffusion

- Vacancy diffusion in 86 runs:
  - Single step, then annihilation: 56
  - Flickers until annihilation: 30

⇒ Vacancy diffusion not relevant, enough other defect modes.

Ion-damaged crystalline silicon

Experiment

Nanocalorimetry on ion-damaged silicon.

- 330 nm thick crystalline silicon strip.
- Implanted with Si^-, 10–100 keV.
- Heated at $10^5\,K\,s^{-1}$.
- Measure heat release.

Simulation

MD+kART:

- 3 keV Si atom into 100 000-atom slab of SW Si (300 K, Langevin bath).
- Cut out 27 000 atoms with defects, PBC.
- Sample kART trajectories.
- Calculate heat release at constant T, transform.

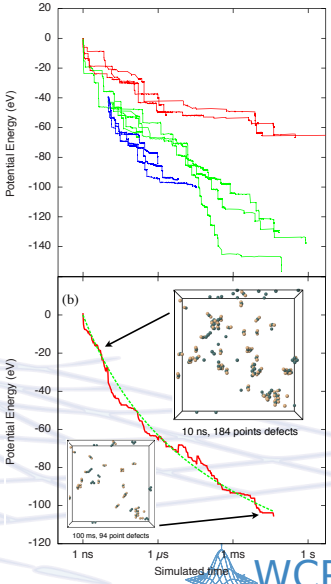
Result

kART simulations

- 3 MD implementation runs
- 3 kART trajectories for each MD.
- Bottom: Average.
- Green: Fit of event distribution.

Replenish and relax:

- Logarithmic relaxation.
- High barrier events: Not necessarily large relaxation.
- But: Access to new areas of configuration space, from which further relaxation possible.
- High barriers: Structural rearrangements.

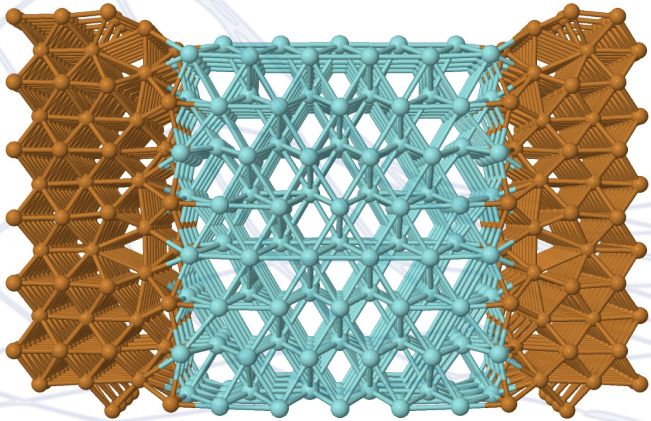


Cu–Zr interface

k-ART for alloy systems

Kinetic ART can also be applied alloy systems.

- Example: Vacancy dynamics near Cu–Zr interface.



K-ART simulations of Cu–Zr

Cu-Zr system

Test simulations:

- 976 atoms (624 Cu, 352 Zr); 5824 atoms (3648 Cu, 2176 Zr).
- Cu 110 on Zr $11\bar{2}0$ (minimal lattice mismatch).
- 1 vacancy at different distance from interface.
- EAM effective potential: Cheng *et al.*, PRL 102, 245501 (2009).

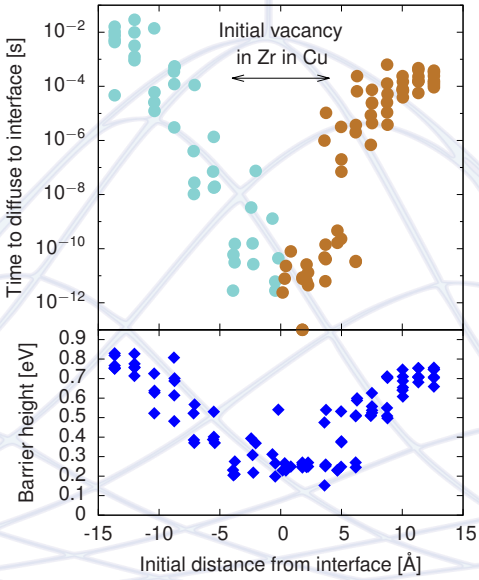
Kirkendall effect

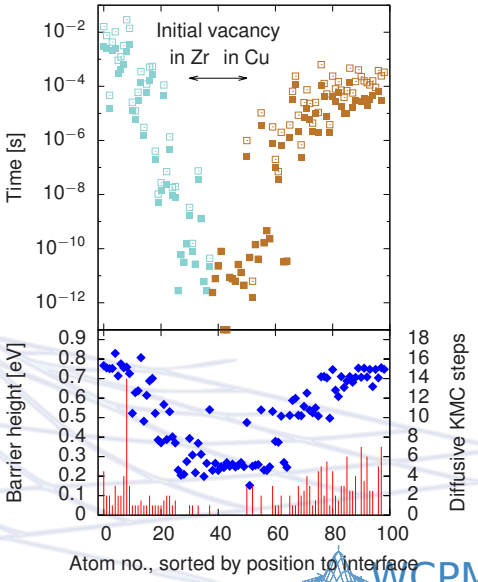
Difference in diffusivity between metals at metal/metal interface

- Interface moves.
- Kirkendall voids at interface.

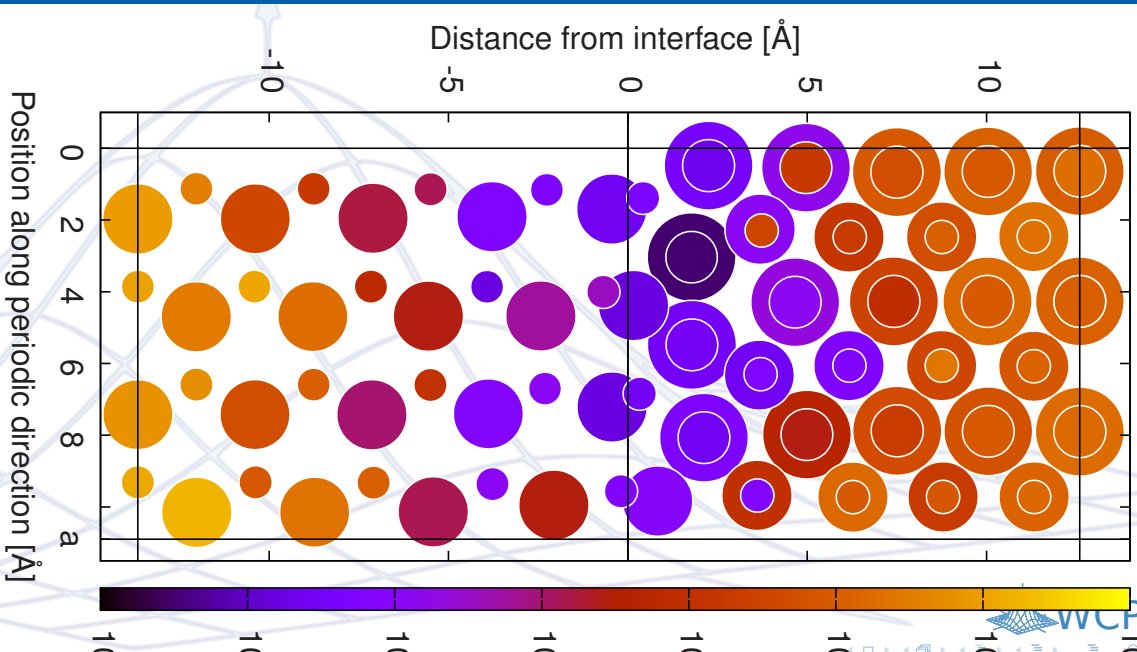
Test simulations: can k-ART do that?

Diffusion time to interface





Diffusion time from each site



Conclusions

Kinetic Activation-Relaxation Technique (k-ART)

Versatile KMC simulation tool for complex systems:

- Off-lattice, self-learning: Few prerequisites.
- Fully account for long-range elastic effects.
- Can handle feature-rich defect systems.
- Basin treated with bac-MRM.
- Even fully amorphous systems.

El-Mellouhi *et al.*, *Phys. Rev. B* **78**, 153202 (2008).
Béland, Brommer, *et al.*, *Phys. Rev. E* **84**, 046704 (2011).

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Calcul Québec

Thank you for your attention!

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