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

Peter Brommer

Département de Physique and
Regroupment Québécois sur les Materiaux de Pointe (RQMP)
Université de Montréal

Beyond Molecular Dynamics: Long Time Atomic-Scale Simulations
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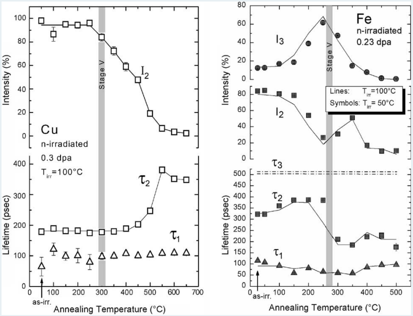
Point defect complexes

Motivation

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

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



- 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
   - Basin treatment

2. Applications
   - Vacancies in α-iron
   - Amorphous silicon

3. Conclusions

The kinetic Activation-Relaxation Technique

KMC method

Execute events according to KMC rules.

off-lattice

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

self-learning

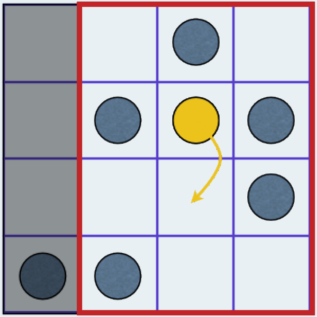
- ART nouveau (fastest unbiased saddle point search) to generate events
  - on the fly
  - corrected for long-range effects.
- Store events: Build topology-based catalog.

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

Kinetic Monte Carlo

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

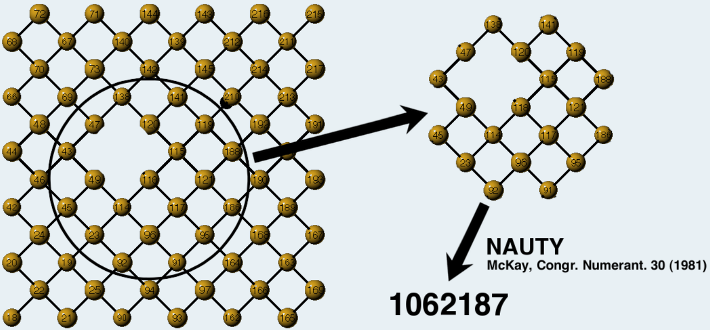
- Predefined, limited catalogue of known events at $T = 0$.
- Ignores long-range interactions between defects.

Cluster centered on each atom

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

⇒ 1:1 relationship between keys and local structures.

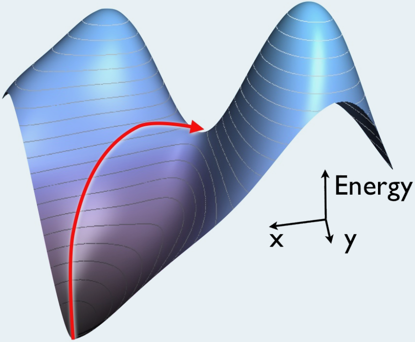
Search for events for each topology.



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

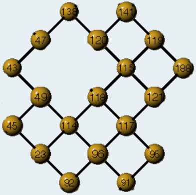
- Calculate rates $r_i = r_0 \exp(\Delta E_i / k_B T)$, $r_0 = 10^{13}\ \mathrm{s}^{-1}$.
- Use tree to select event with proper probability.

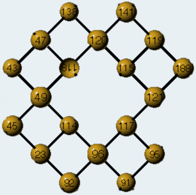
Reconstructing events

Geometric transformation

Stored event

initial





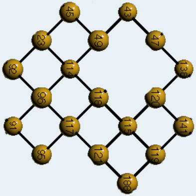
final

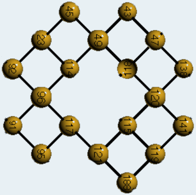
- Extract symmetry operation needed to transform stored event to configuration.

$\Leftarrow$ $\Rightarrow$

- Apply same operation to final (saddle) state.

Configuration





rotate 90 degrees.

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:

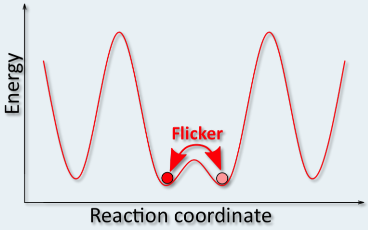
- Old ones removed.
- New ones calculated.

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

bac-MRM

Local configurations with low barriers

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



Requirements

- Correct distribution of exit states.
- Low overhead.

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

de Montreal

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.

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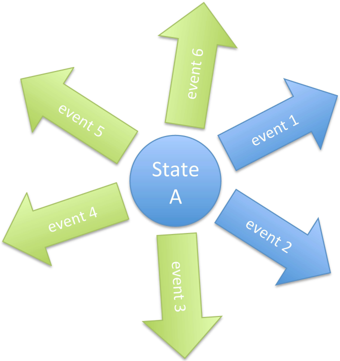
The Basin Mean Rate Method

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.

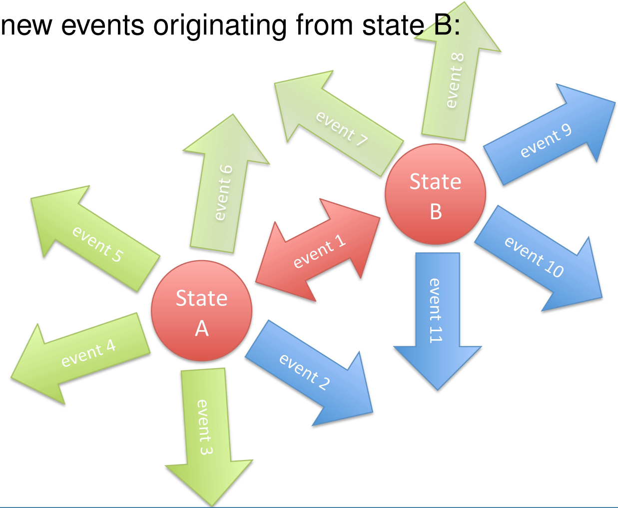


Legend

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.
- 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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Outline

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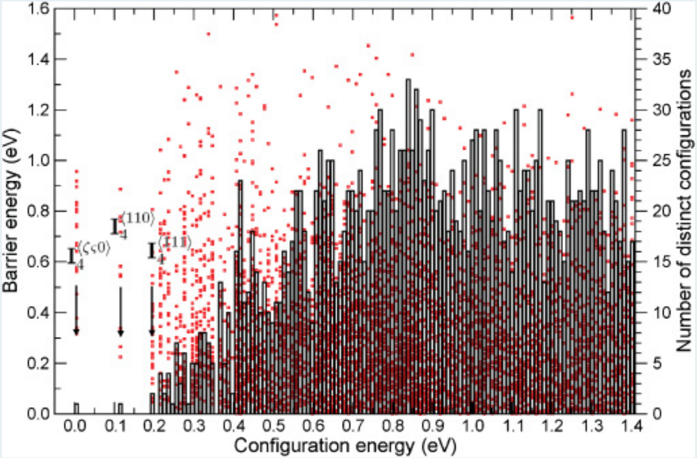
Atomistic simulation of α-Fe: Challenges

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

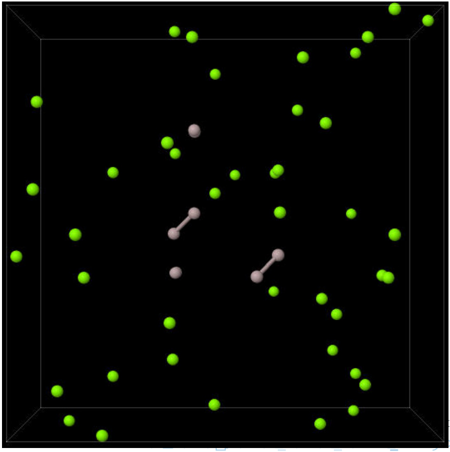
- Slower dynamics than interstitials.
- PAS results available.

The system: 2000 atoms

Remove 50 random atoms.

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

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



K-ART simulations at 50 °C.

Cluster growth

Average size > 6

- 0.1 ms

Time scale

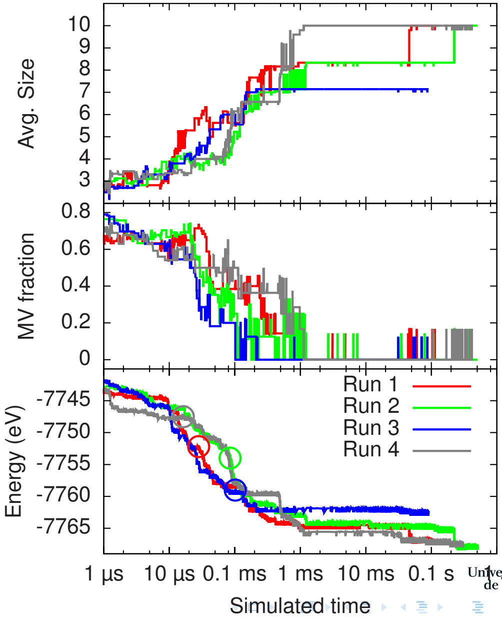
Vacancy clustered:

- 1 ms

Energy barriers

Maximal eff. barrier:

- 0.8–1.1 eV



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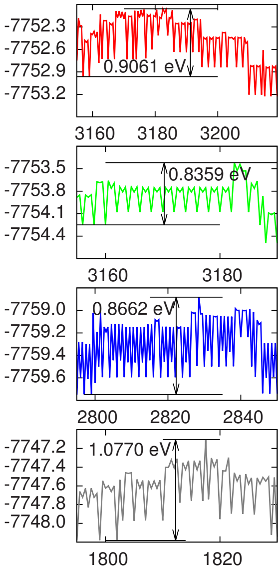
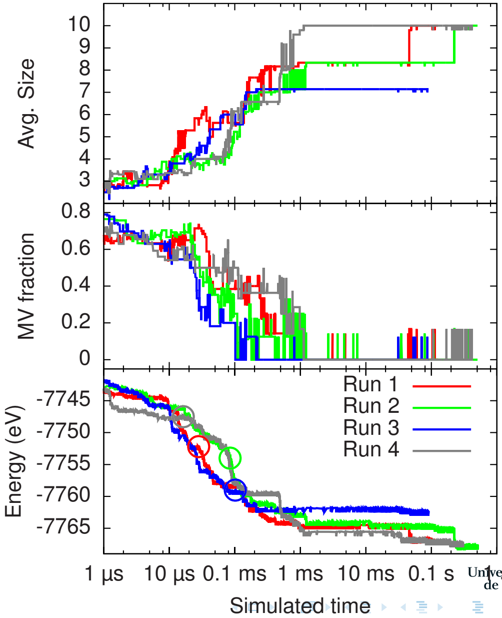
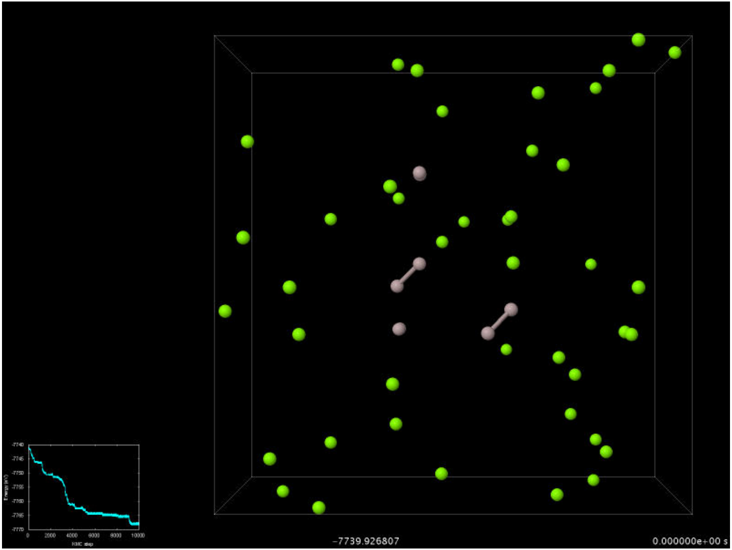
K-ART simulations at 50 °C.





50 vacancies in α Fe



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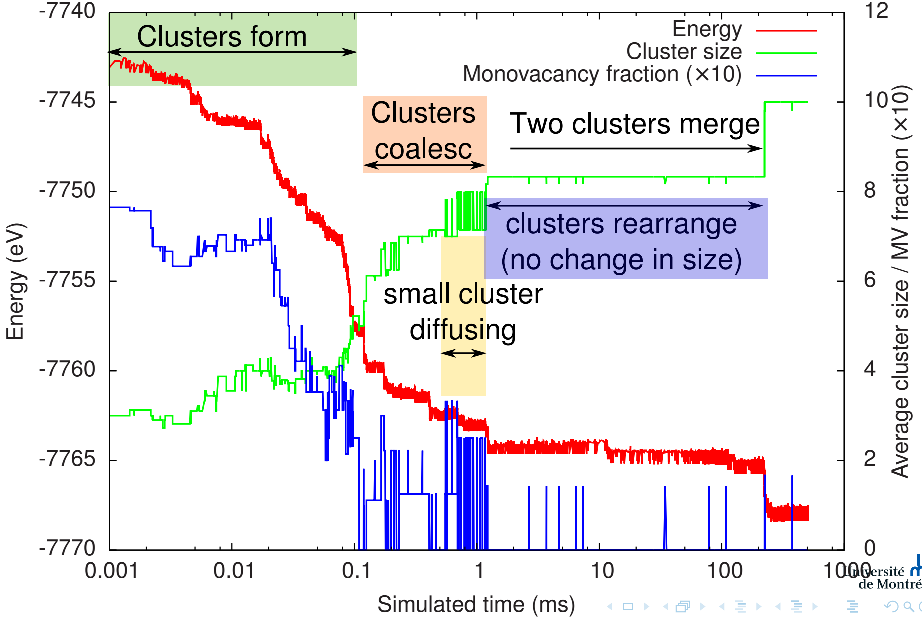
Trajectory in detail



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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)

⇒ k-ART simulation agrees with experiment

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

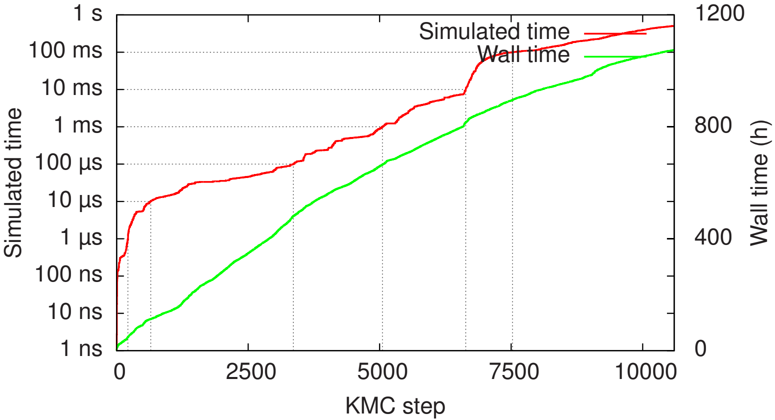
Previous results: Autonomous Basin Climbing

- 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)

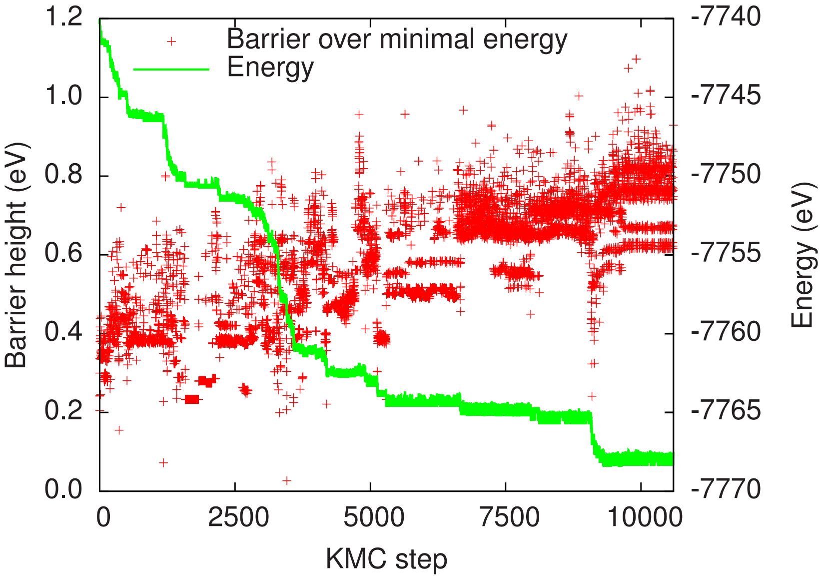
Accelerating simulation



Reasons

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

Executed event barrier



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Increasing basin threshold

Basin acceleration with bac-MRM

Basin auto-constructing Mean Rate Method:

- "Low" barriers: Average over transitions.
- Expand basin on the fly.
- Correct distribution of exit states.
- Parameter: Basin threshold.

Optimal basin threshold

There is an optimal value for the basin threshold:

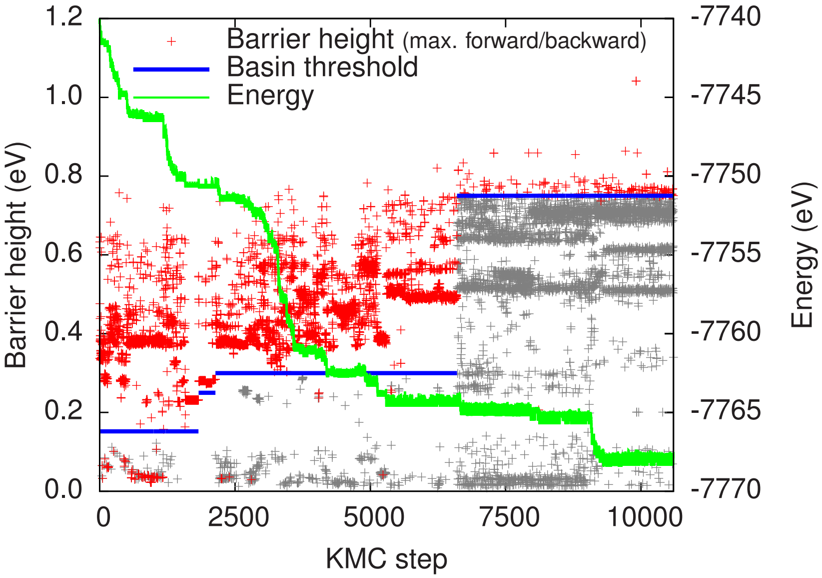
Too low: No progress.

Too high: Too many states in basin:

- Lose trajectory
- Memory requirements.

Gradual increase during simulation.

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.

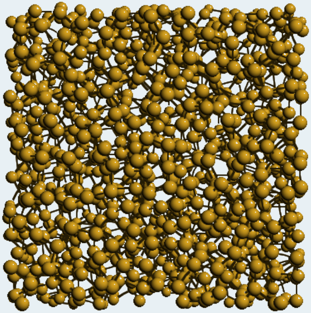
Amorphous silicon

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).

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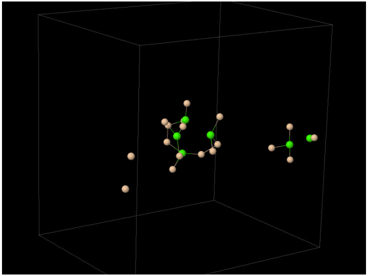
k-ART simulation of a vacancy in a-Si

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.

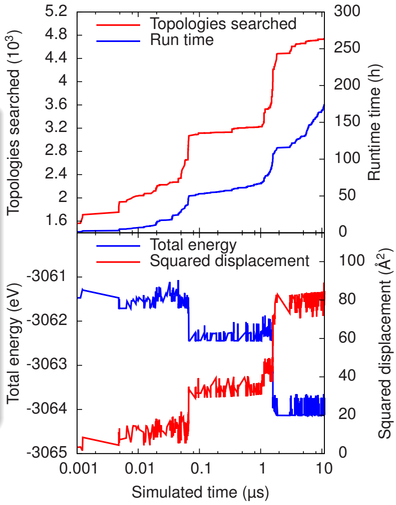


Results: Vacancies in a-Si

200+ kART runs

- Most of them: Vacancy disappears
  - in initial minimization
  - or first few steps (ns).
- Rarely:
  - Vacancy stable over 1–100 µs.
- Even rarer: Vacancy diffusion.

Ongoing work: Longer/more simulations



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Outline

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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