Transition states and where to find them

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Motivation

Long-time low-temperature evolution

Infrequent events:

- Rare diffusive events propagate system (µs. . . ms. . .).
- Still need to integrate out thermal vibrations (fs).

Time-scale problem.

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Time-scale problem.

State-to-state trajectory

Direct simulation of diffusive events.

- Avoid integrating out thermal vibrations.
- No direct coupling between models.

Kinetic Monte Carlo

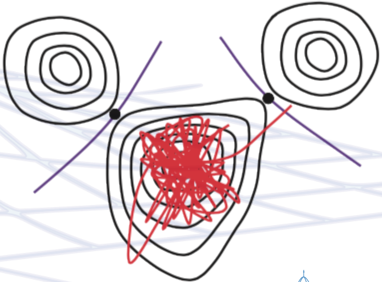


Image: Voter, Radiat. Effects Solids, 2007, 235, 1

Outline

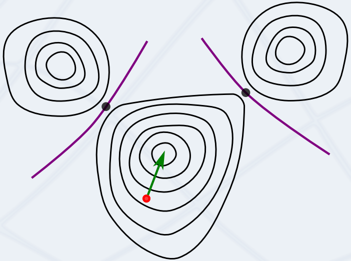
1. Kinetic Monte Carlo
2. Transition State Search
   - Aside: Dimer method
3. Implementation: kART

Kinetic Monte Carlo - the premise

What is a state?

Continuously take trajectory snapshots and relax to (local) minimum.

- Minimum:
- Initial state.

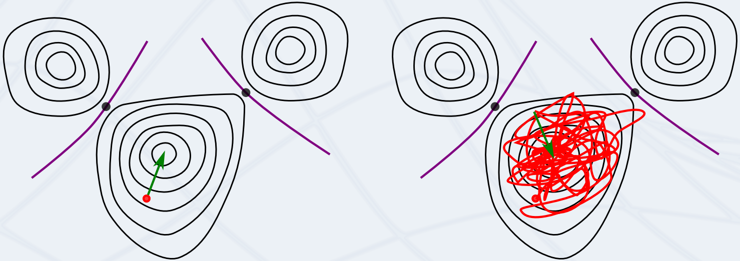


Kinetic Monte Carlo - the premise

What is a state?

Continuously take trajectory snapshots and relax to (local) minimum.

- Minimum:
- Initial state.
- Run MD.
- Return to same state.



Kinetic Monte Carlo - the premise

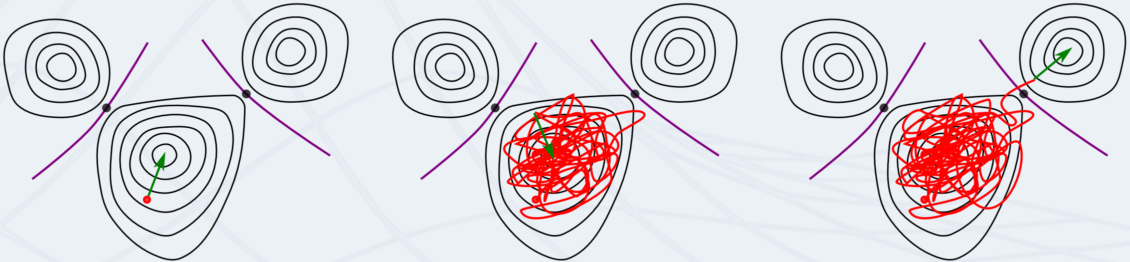
What is a state?

Continuously take trajectory snapshots and relax to (local) minimum.

- Minimum:
- Initial state.

- Run MD.
- Return to same state.

- More MD.
- Distinct state.



Trajectory (and state): Configuration space.

Entire system moved from state to state.

Transition Rates

State to state trajectory

System stays in state long enough to lose all “memory”.

- Rate constant k_{ij} for system in state i to escape to j
- Depends only on shape of basin i (and maybe j), ridge ij, not previous states!

Defining property of Markov chain $\Rightarrow$ Easy to get trajectory from $\{k_{ij}\}$.

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Escape time

Constant probability of escape: Exponential decay $p_{\text{survival}}(t) = \exp(-k_{\text{tot}}t)$, $k_{\text{tot}} = \sum_j k_{ij}$.

- Probability distribution of time to first escape: $p(t) = k_{\text{tot}} \exp(-k_{\text{tot}}t)$.
- Average time $\tau = \int_0^\infty t\, p(t) dt = \frac{1}{k_{\text{tot}}}$.
- Sample from time distribution: $\Delta t = -(1/k) \ln(r), 0 < r < 1$.

Pick event according to rates.

Transition State Theory

Ensemble averages

Rate k_{ij} to go from state i to j.

- Equilibrium flux through dividing surface.
- In ensemble, count forward crossings per unit time, divide by # in i.
- Correct for correlated re-crossings (particularly if bad dividing surface).
- 1D, dividing surface at $x = 0$: $k_{ij}^{\mathrm{TST}} = \langle |dx/dt| \delta(x) \rangle_i$.

In practice never done this way.

Harmonic Transition State Theory

Transition pathway characterised by saddle points

- Reaction coordinate: direction of normal mode with imaginary frequency.

$\Rightarrow$ Negative eigenvalue!

- Dividing surface: Saddle plane (hyperplane $\perp$ reaction coordinate).
- Basin: described by second order expansion (harmonic vibration).
- Saddle: same for modes $\perp$ reaction coordinate.

$$k^{\text{HTST}} = \frac{\prod_{i}^{3N} \nu_i^{\text{min}}}{\prod_{i}^{3N-1} \nu_i^{\text{sad}}} \exp(-E_{\text{static}}/k_B T).$$

- Frequent approximation: assume all ν_i equal.

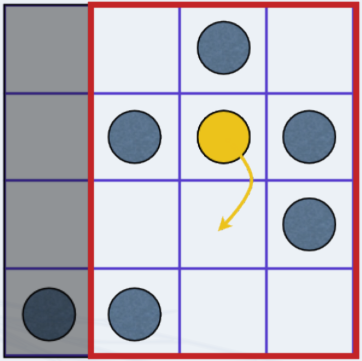
$$k = k_0 \exp(-E_{\text{static}}/k_B T).$$

$\Rightarrow$ Only requires knowledge of static barrier height E_{static}.

Kinetic Monte Carlo

Standard KMC

- Problem must be lattice based.
- List of possible events is constructed
- Find saddle point with e.g. Nudged Elastic Band.
- Limited amount of neighbours included.
- Catalog size grows exponentially with number of neighbours.



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.

Calculating rates without lattice

Find saddle points without knowing final state

Not as easy as “go uphill”.

- Dimer method (Henkelman and Jónsson, J. Chem. Phys. **115**, 9657 (2001)).
- ART nouveau (Barkema, Mousseau, PRL 77 (1996);Malek, Mousseau, PRE 62 (2000);)
- …

Key point: Find the lowest eigenvalue and follow eigenvector out of basin.

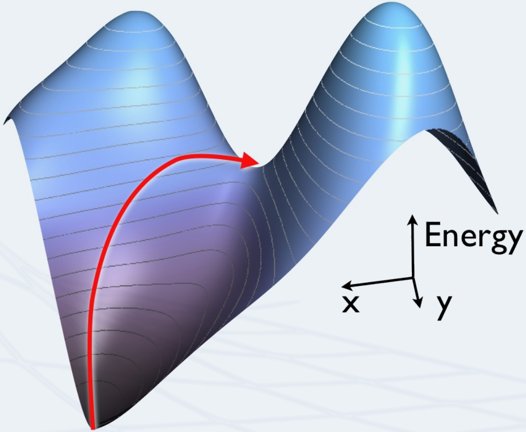
ART nouveau

Method implemented in kART.

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.

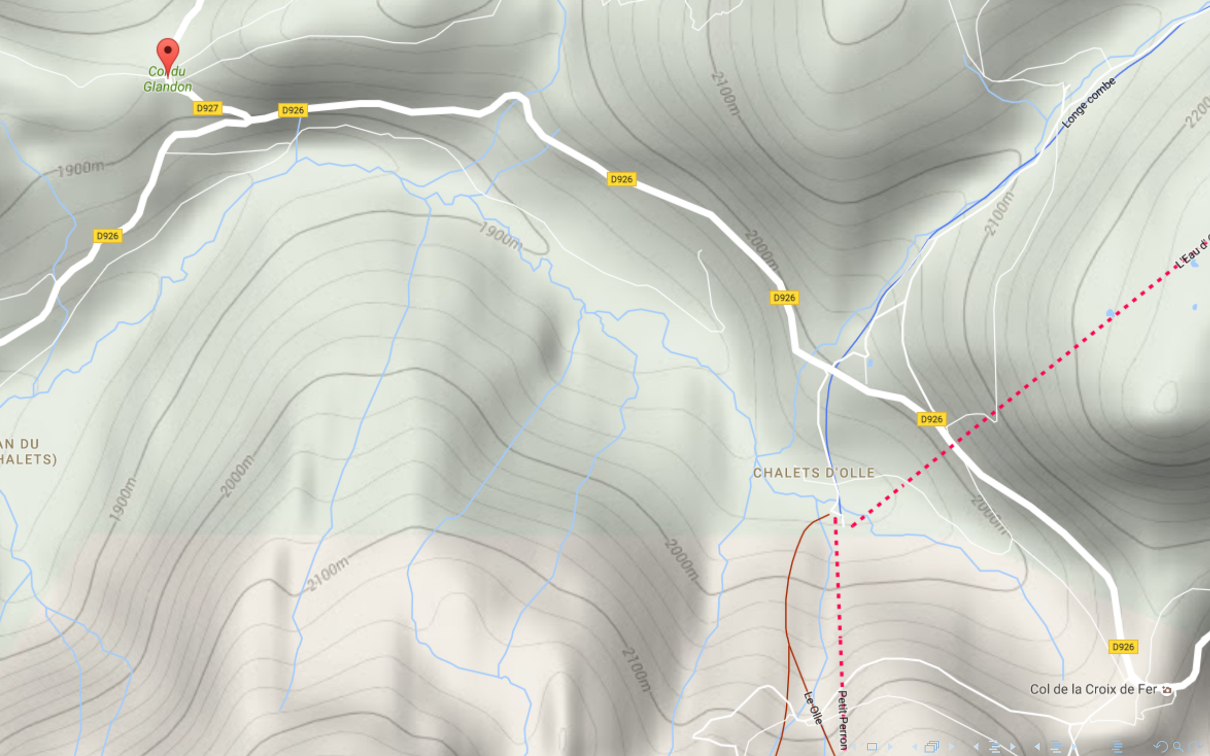


5. Move configuration over the saddle point and relax to new minimum.

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

Step 1: Leaving the harmonic basin

Tempting to use Hessian matrix at minimum


Col du Glandon
D927
D926
1900m
2000m
2100m
Longe combe
CHALETS D'OLLE
Col de la Croix de Fer
Le Olle
Petit Perron

Step 1: Leaving the harmonic basin

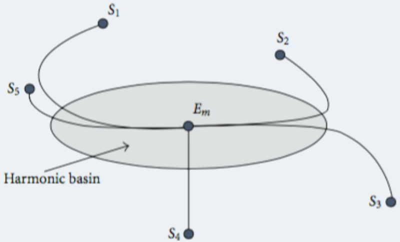
Tempting to use Hessian matrix at minimum

However, most trajectories from saddle points join single (softest) mode.

- No discriminating basis.

⇒ Use random displacements

Image: Mousseau *et al.*, JAMOP, **2012**, 925278 (2012)



Random initial displacements

System state is an all atom description.

- All-atom random displacements oversample most favourable events.
- Displace local environments, let rest react to displacement.
- Use Lanczos to evaluate lowest eigenvalue. If sufficiently negative: out of basin.

Cheaper sampling of all events.

Step 2: Up towards the saddle point

Lanczos Method

Iterative method to find lowest eigenvalues of a matrix.

- Not interested in all eigenvalues, only lowest ones.
- Use with “small” set (15...4) of Lanczos vectors (4 needs monitoring).
- Push along negative eigendirection, do some minimisation $\perp$.
- Iterative: Cut down on cost of updating Lanczos.

DIIS (direct inversion in iterative subspace)

DIIS is unselective

- Will find any special point (minimum, maximum, saddle).
- Cheaper.
- Sensitive to roughness.

Cheaper convergence to saddle point in some systems.

Step 3: Downhill again.

The simple part

Just make a small step "forward" and minimise from there.

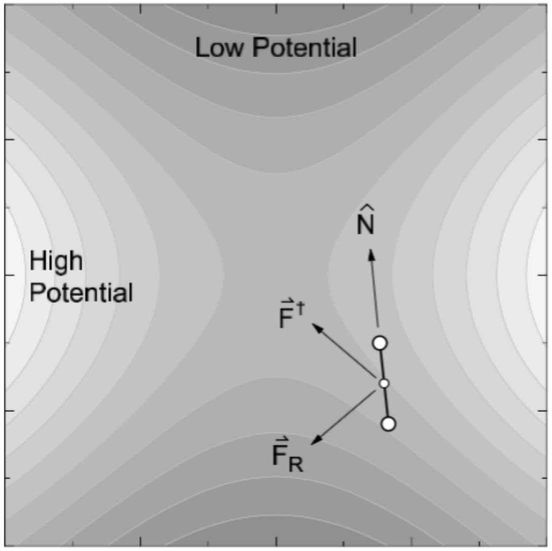
Dimer Method

Easier to visualise

Use a pair of images (dimer)

- Rotate to minimise energy.
- Calculate force on dimer.
- Flip component $\parallel$ dimer.
- Converge to saddle point.

Henkelman *et al.*, in Progress on Theoretical Chemistry and Physics, Ed. S. D. Schwartz, 269-300 (Kluwer, 2000).



Computational cost

How many force evaluations per saddle point?

Contentious point between methods: Measure of efficiency.

- Generally: $10^{2.5}$, almost independent of DoF.
- If accounting for failed events: 300...1000.

More important: How many searches to find all ("significant") barriers?

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Kinetic Activation-Relaxation technique (kART)

Self-learning, off-lattice Kinetic Monte Carlo (adaptive KMC)

Combine ART nouveau with:

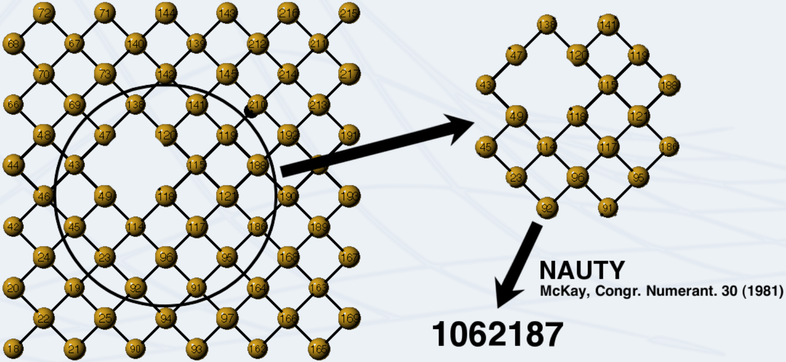
- off-lattice atom classification scheme
- event database
- long-range corrections
- KMC framework.

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.



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.

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).

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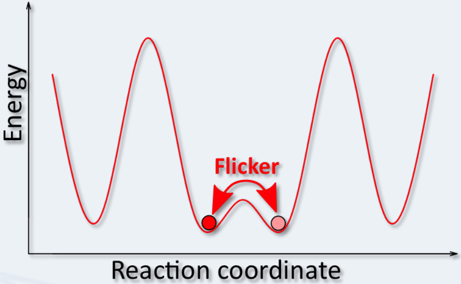
Local configurations with low barriers

- 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)

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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