Méthodes cinétiques :
Monte Carlo cinétique, Paysage énergétique, Activation Relaxation Technique

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KINETIC MODELING METHODS

Approaches used to describe and predict the temporal evolution of dynamic systems, particularly in chemistry, biology, and physics.

- Reaction Order Models
- Transitional Phase Kinetics
- Molecular Dynamics

KINETIC MONTE CARLO

Motivation
Fundaments
Algorithm
…

INGREDIENTS

Activation barrier
Reaction rate

Exploration of the Potential Energy Surface

Activation Relaxation Technique
ARTn

Journal of Chemical Theory and Computation **16** (2020) 6726-6734 - *doi:* 10.1021/acs.jctc.0c00541

Caractériser les cinétiques des diffusions atomiques avec la technique d'activation relaxation - Techniques de l'Ingénieur RE-192 - 2023

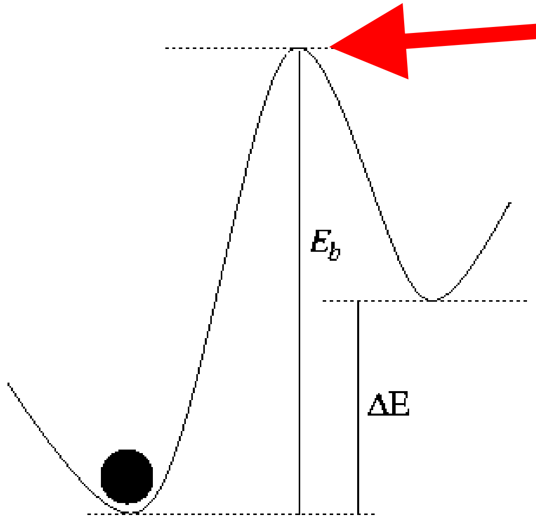
Computer Physics Communication 295 (2024), 108961, doi: https://doi.org/10.1016/j.cpc.2023.108961

Part II – Antoine JAY

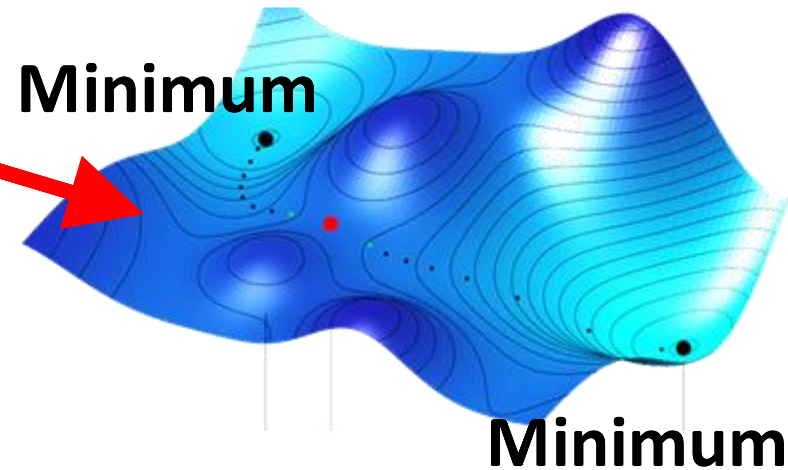
2. ACTIVATED EVENTS

POTENTIAL ENERGY SURFACE & TRANSITION STATE THEORY

- **Transition State Theory** is an approach for modeling the rate of chemical reactions based on the idea of a transition state or activated complex.
  → The chemical reaction = a process where the reactants cross an energy barrier to form products. This barrier is associated with a transition state where the reactants are transformed into products.



Transition State



Reaction rate

$$k_{i\to j} = \nu \times e^{-\frac{E_b}{kT}}$$

Thermodynamics: We need to sample correctly the phase space and access all relevant points in phase space and probability

Kinetics: we need to establish the dynamical evolution of the system and describe accurately the dynamical relation between points in phase space

3. KINETIC MONTE CARLO

WHAT ARE WE INTERESTED IN?

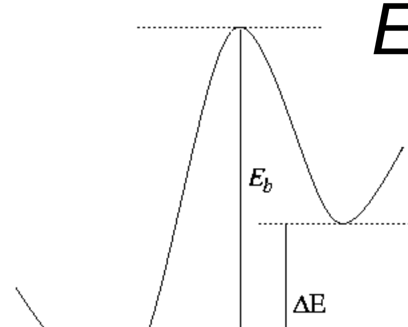
Game of chance

> Monte Carlo
- Random Number to perform events
  - ➢ Statistical method

> Kinetic
- Transitions between discrete states over time
- TST & activation barrier
  - ➢ Probabilistic method

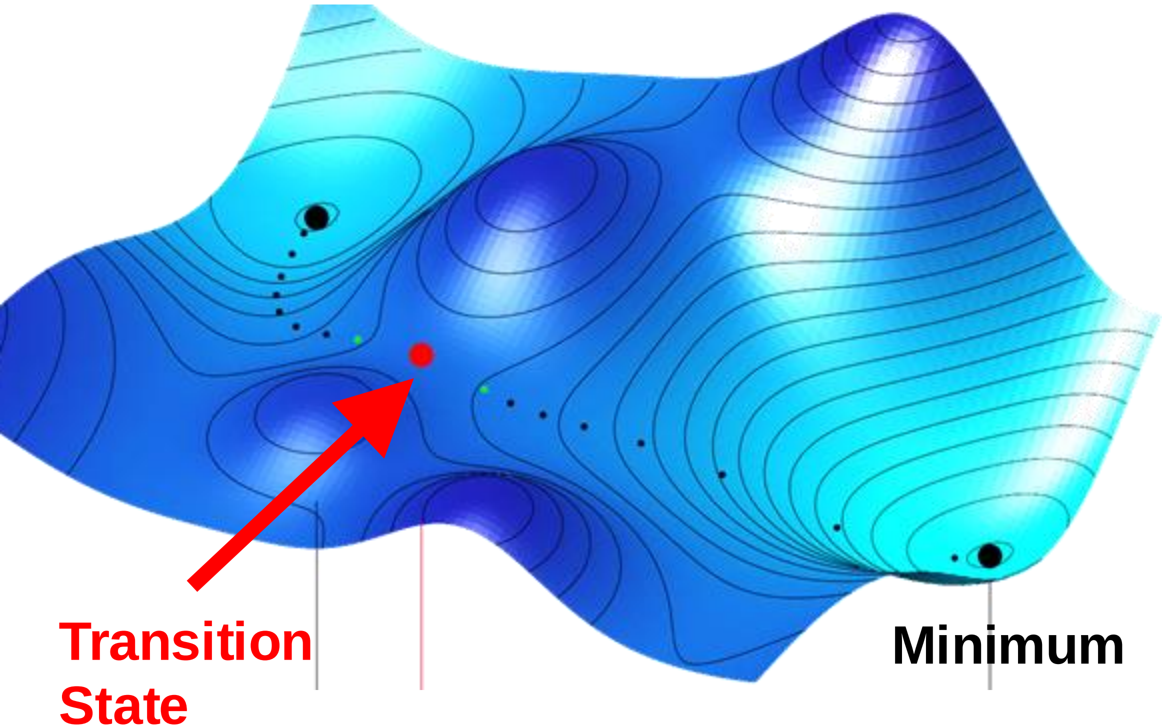
Transition State Theory

$E_b \; \alpha \; t$



The kinetic Monte Carlo method allows for simulating the temporal evolution of a system in discrete steps based on random sampling

> Density Functional Theory based calculations



- Electronic structure of material
- Minimum configuration
- Relaxation
- ➢ DFT helps to identify the ground state
- Specific algorithms
- ➢ DFT characterization of the TS

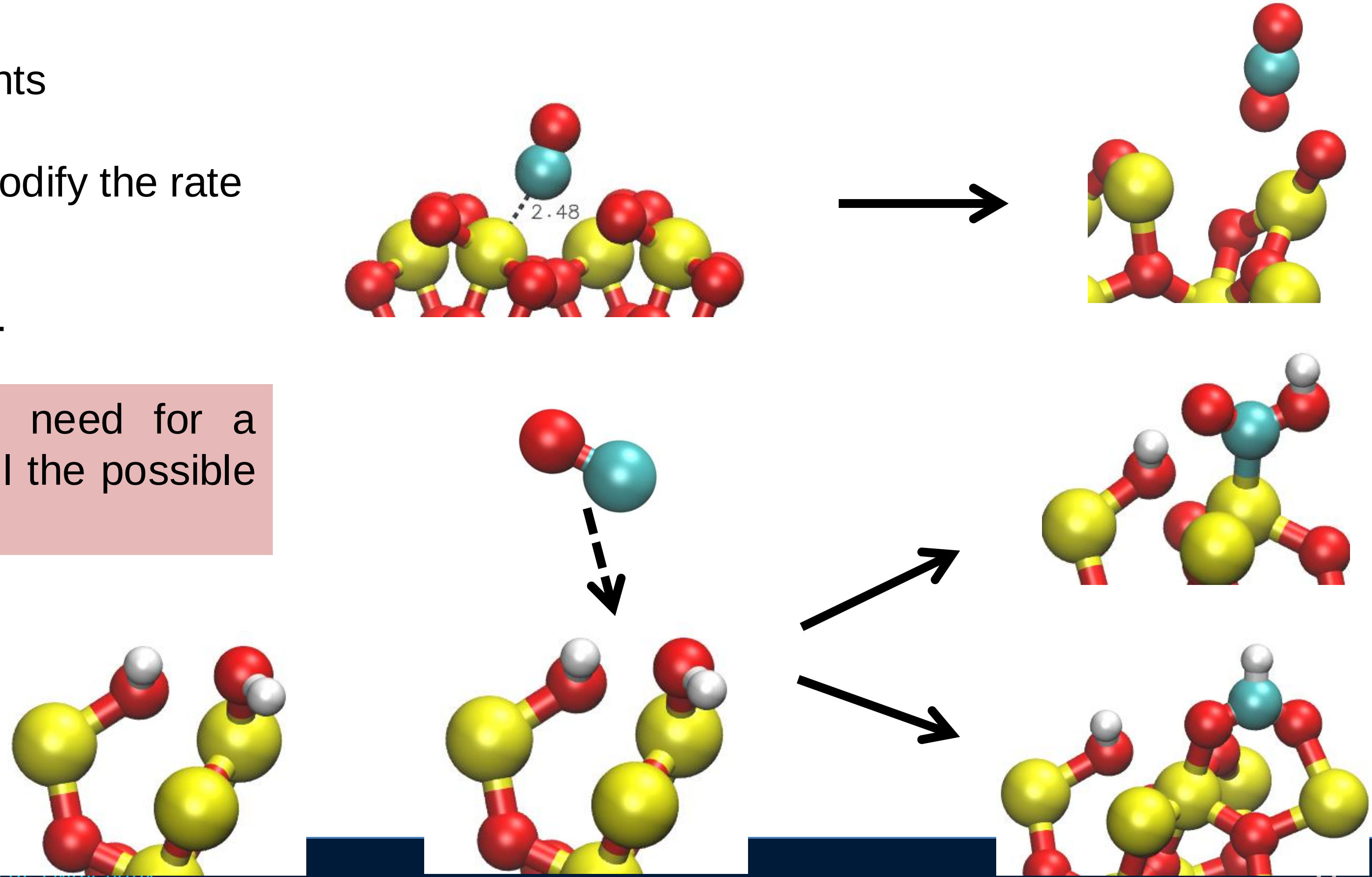
> Density Functional Theory based calculations

CO adsorption on SnO2

- Parallel atomic events
- Competitive events
- Coverage effects modify the rate

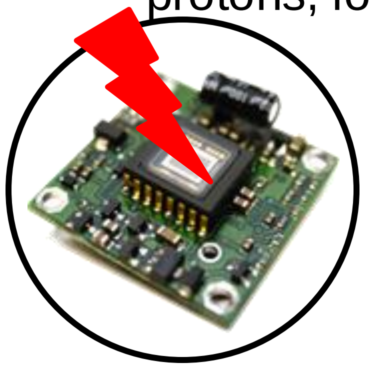
- Effects of P and T…

DFT is not enough, need for a method to consider all the possible events, mix them



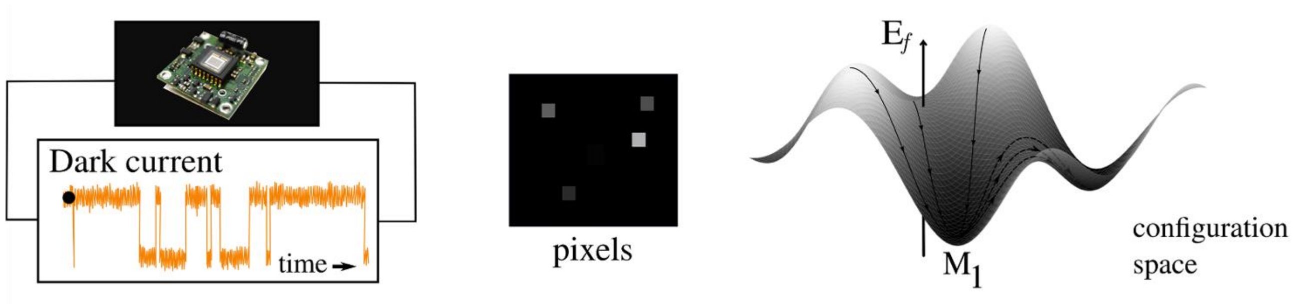
> # Molecular Dynamics

protons, ions

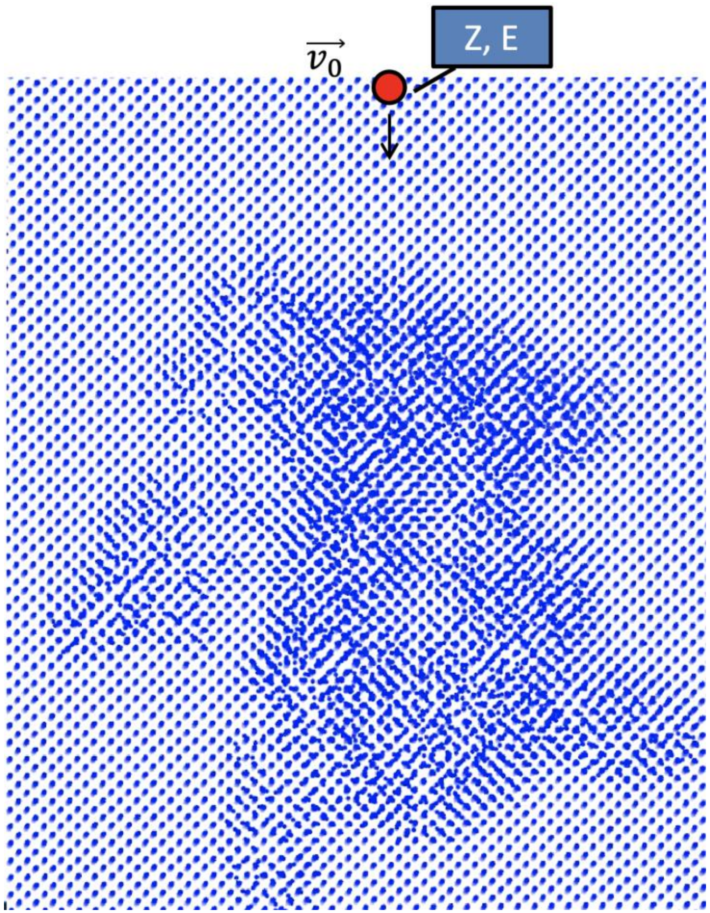


Silicon-based image sensor

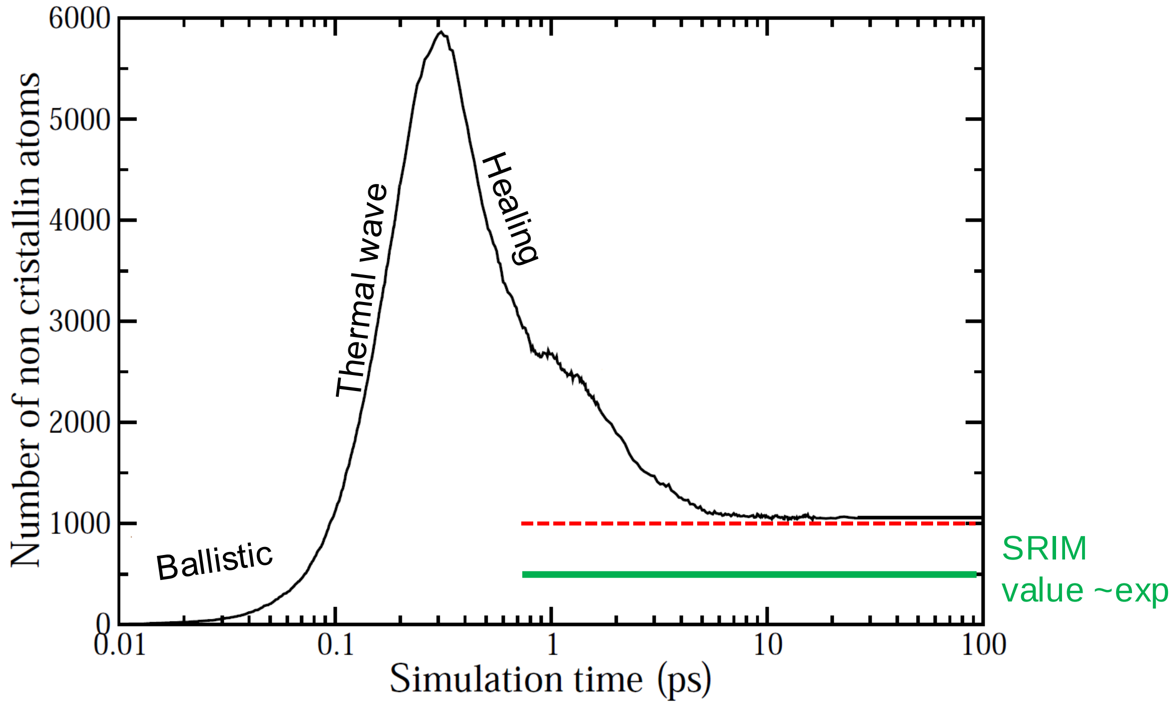
Random Telegraph Signal



> ## Molecular Dynamics



> ## Evolution of the number of defects

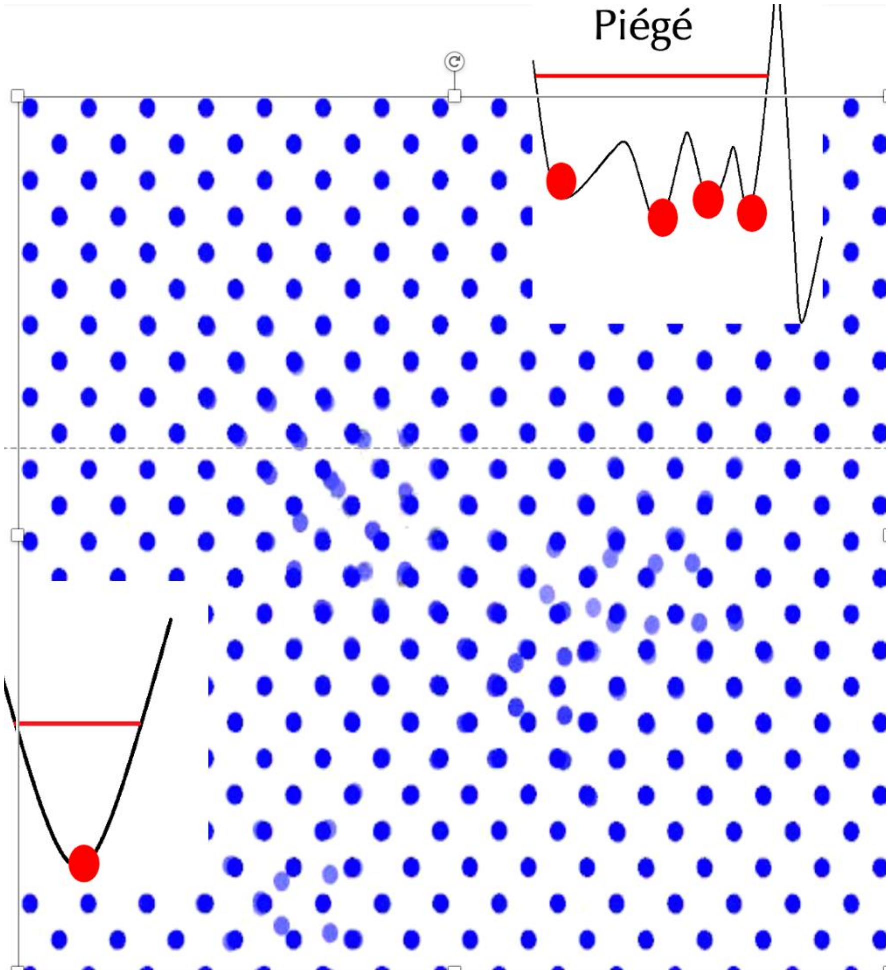


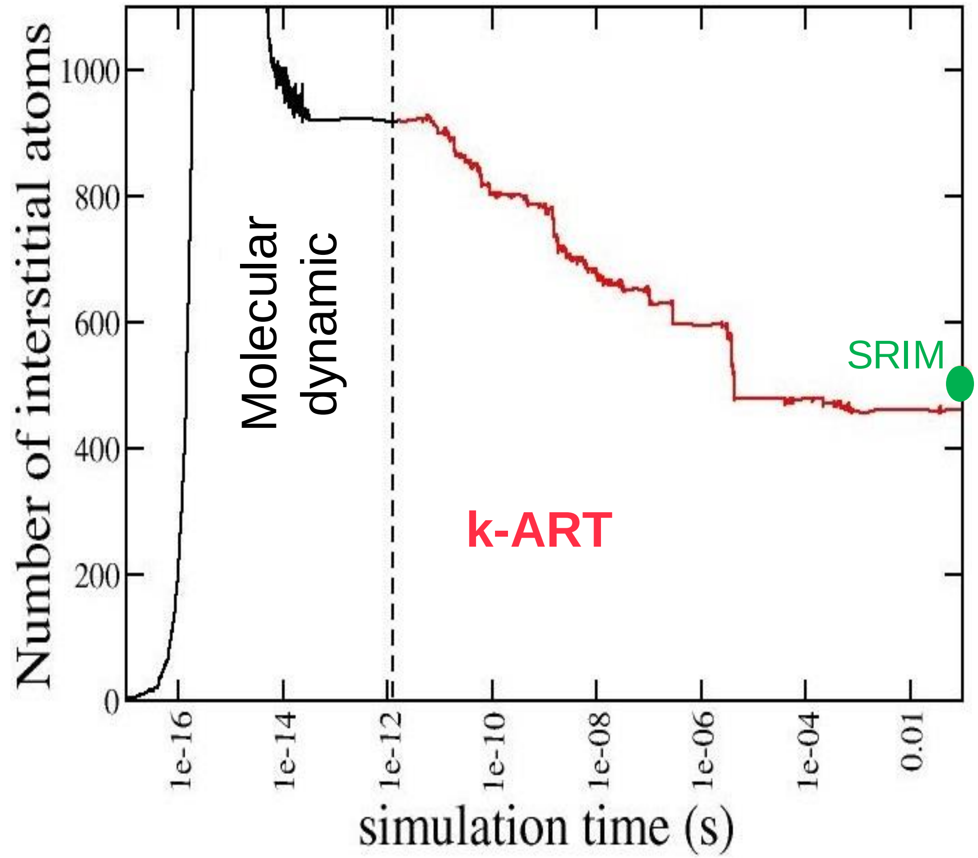
Limitation of the Molecular Dynamics

What to do next with those defect structures ?

➢ Need to access to longer times (seconds or more)

> Output of Molecular Dynamics → kinetic ART (code KMC)



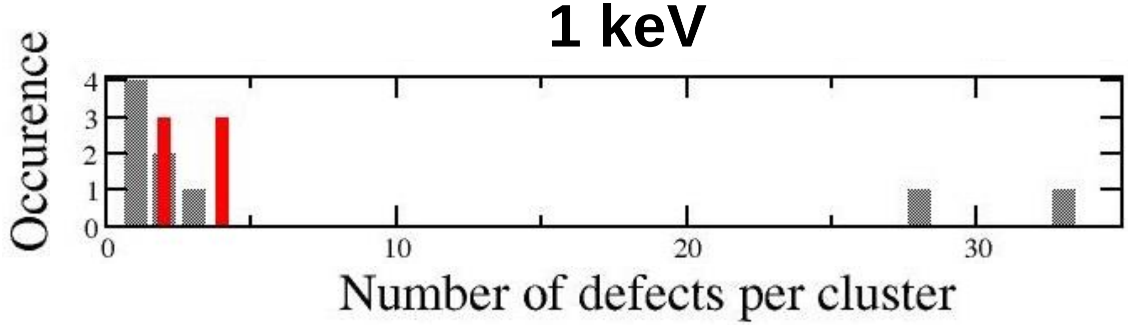


> Output of Molecular Dynamics → kinetic ART (code KMC)

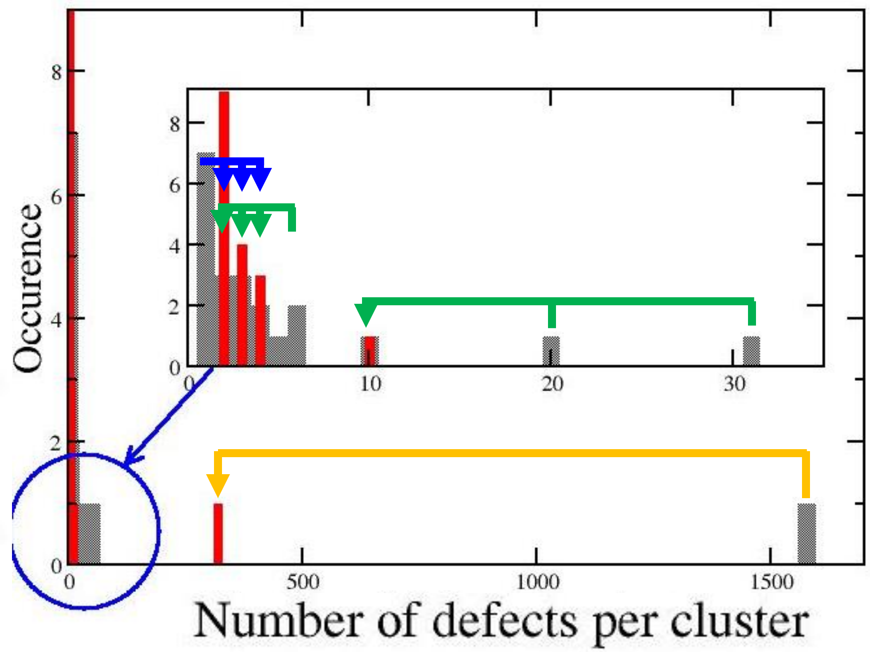
At the end of the MD simulation (1 ns)

At the end of the k-ART simulation (1 s)

1 keV



10 keV



Large Sized Clusters (100 keV):
Partial healing

Medium Sized Clusters:
Healing

Point defects:
Diffusion + Agglomeration into small clusters or Recrystallisation

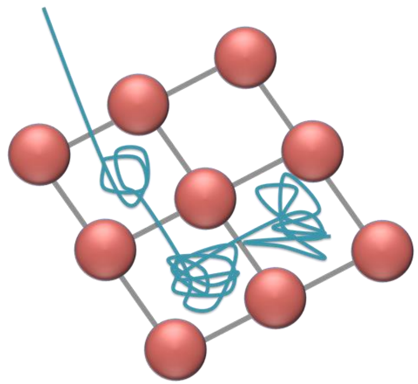
3. KINETIC MONTE CARLO

WHY DO WE NEED KMC?

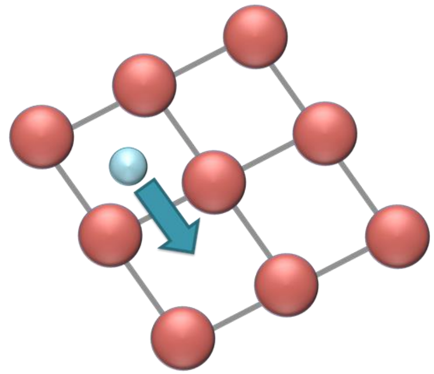
> Lifetime of events as a function of T and activation barrier

	Temp (K)	50	100	200	300	400	500	600	700	800	900	1000
	Energy (eV)											
	0.1	1.20E-003	1.10E-008	3.31E-011	4.79E-012	1.82E-012	1.02E-012	6.92E-013	5.25E-013	4.27E-013	3.63E-013	3.19E-013
	0.2	1.44E+007	1.20E-003	1.10E-008	2.29E-010	3.31E-011	1.04E-011	4.79E-012	2.75E-012	1.82E-012	1.32E-012	1.02E-012
	0.3	1.73E+017	1.32E+002	3.63E-006	1.10E-008	6.02E-010	1.06E-010	3.31E-011	1.45E-011	7.76E-012	4.79E-012	3.25E-012
	0.4	2.08E+027	1.44E+007	1.20E-003	5.24E-007	1.10E-008	1.08E-009	2.29E-010	7.58E-011	3.31E-011	1.74E-011	1.04E-011
	0.5	2.50E+037	1.58E+012	3.98E-001	2.51E-005	1.99E-007	1.10E-008	1.58E-009	3.98E-010	1.41E-010	6.31E-011	3.31E-011
	0.6	3.00E+047	1.73E+017	1.32E+002	1.20E-003	3.63E-006	1.12E-007	1.10E-008	2.09E-009	6.02E-010	2.29E-010	1.06E-010
	0.7	3.60E+057	1.90E+022	4.36E+004	5.75E-002	6.60E-005	1.14E-006	7.58E-008	1.10E-008	2.57E-009	8.31E-010	3.37E-010
	0.8	4.33E+067	2.08E+027	1.44E+007	2.75E+000	1.20E-003	1.16E-005	5.24E-007	5.75E-008	1.10E-008	3.02E-009	1.08E-009
	0.9	5.20E+077	2.28E+032	4.78E+009	1.32E+002	2.19E-002	1.18E-004	3.63E-006	3.02E-007	4.67E-008	1.10E-008	3.43E-009
	1	6.25E+087	2.50E+037	1.58E+012	6.30E+003	3.98E-001	1.20E-003	2.51E-005	1.58E-006	1.99E-007	3.98E-008	1.10E-008
	1.1	7.50E+097	2.74E+042	5.23E+014	3.01E+005	7.23E+000	1.22E-002	1.74E-004	8.31E-006	8.51E-007	1.44E-007	3.50E-008
	1.2	9.01E+107	3.00E+047	1.73E+017	1.44E+007	1.32E+002	1.25E-001	1.20E-003	4.36E-005	3.63E-006	5.24E-007	1.12E-007
	1.3	1.08E+118	3.29E+052	5.74E+019	6.90E+008	2.39E+003	1.27E+000	8.31E-003	2.29E-004	1.55E-005	1.90E-006	3.56E-007
	1.4	1.30E+128	3.60E+057	1.90E+022	3.30E+010	4.36E+004	1.29E+001	5.75E-002	1.20E-003	6.60E-005	6.91E-006	1.14E-006
	1.5	1.56E+138	3.95E+062	6.29E+024	1.58E+012	7.93E+005	1.32E+002	3.98E-001	6.30E-003	2.82E-004	2.51E-005	3.63E-006
	1.6	1.87E+148	4.33E+067	2.08E+027	7.57E+013	1.44E+007	1.34E+003	2.75E+000	3.31E-002	1.20E-003	9.11E-005	1.16E-005
	1.7	2.25E+158	4.74E+072	6.89E+029	3.62E+015	2.62E+008	1.37E+004	1.90E+001	1.74E-001	5.12E-003	3.31E-004	3.70E-005
	1.8	2.70E+168	5.20E+077	2.28E+032	1.73E+017	4.78E+009	1.39E+005	1.32E+002	9.11E-001	2.19E-002	1.20E-003	1.18E-004
	1.9	3.25E+178	5.70E+082	7.55E+034	8.29E+018	8.69E+010	1.42E+006	9.11E+002	4.78E+000	9.32E-002	4.36E-003	3.76E-004
	2	3.90E+188	6.25E+087	2.50E+037	3.97E+020	1.58E+012	1.44E+007	6.30E+003	2.51E+001	3.98E-001	1.58E-002	1.20E-003
1V	0.23	1.52E+010	3.90E-002	6.25E-008	7.31E-010	7.90E-011	2.08E-011	8.55E-012	4.53E-012	2.81E-012	1.94E-012	1.44E-012
2V	1.1	7.50E+097	2.74E+042	5.23E+014	3.01E+005	7.23E+000	1.22E-002	1.74E-004	8.31E-006	8.51E-007	1.44E-007	3.50E-008
3V	1.6	1.87E+148	4.33E+067	2.08E+027	7.57E+013	1.44E+007	1.34E+003	2.75E+000	3.31E-002	1.20E-003	9.11E-005	1.16E-005
4V	2.58	1.13E+247	1.06E+117	1.03E+052	2.20E+030	3.21E+019	1.01E+013	4.69E+008	3.76E+005	1.79E+003	2.80E+001	1.01E+000
1I	0.16	1.34E+003	1.16E-005	1.08E-009	4.87E-011	1.04E-011	4.10E-012	2.21E-012	1.42E-012	1.02E-012	7.87E-013	6.40E-013
2I	0.25	1.58E+012	3.98E-001	1.99E-007	1.58E-009	1.41E-010	3.31E-011	1.26E-011	6.31E-012	3.76E-012	2.51E-012	1.82E-012
3I	0.48	2.41E+035	1.55E+011	1.25E-001	1.16E-005	1.12E-007	6.89E-009	1.08E-009	2.86E-010	1.06E-010	4.87E-011	2.62E-011
4I	2.29	6.64E+217	2.58E+102	5.08E+044	2.95E+025	7.12E+015	1.21E+010	1.72E+006	3.07E+003	2.67E+001	6.66E-001	3.48E-002
FFCD	2.65	1.28E+254	3.58E+120	5.99E+053	3.30E+031	2.45E+020	5.14E+013	1.82E+009	1.20E+006	4.95E+003	6.91E+001	2.27E+000

> Molecular Dynamics vs KMC



MD: Real trajectory of atomic diffusion



KMC: Discrete jumps

Event in KMC:
- Initial state
- Final state
- Transition state = activation barrier to execute the move

→ MD for short lifetime events

→ KMC for rare events of atom dynamic and significant, not reachable with MD*

*  * high cost

> Ability to simulate processes over much longer timescales than those accessible by molecular dynamics, especially for systems where rare but important events determine the overall system behavior

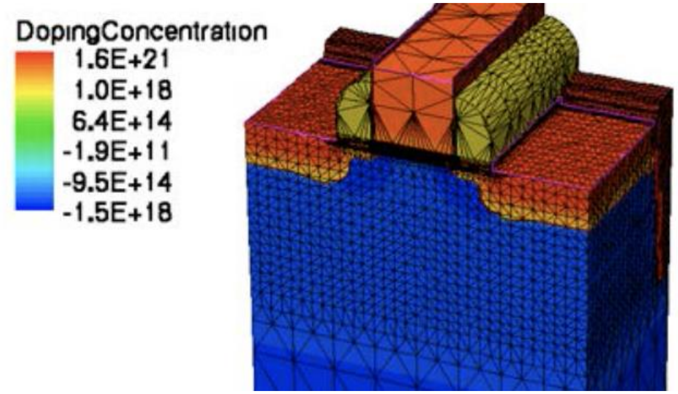
… BIOLOGY, CHEMISTRY, MATERIAL SCIENCE

Surface diffusion
Chemical reactions on catalytic surfaces
Thin film growth
Diffusion in alloys
Defect mobility and clustering in irradiated solids
Dislocation motion
Material engineering …

➢ Methodology of industrial interest

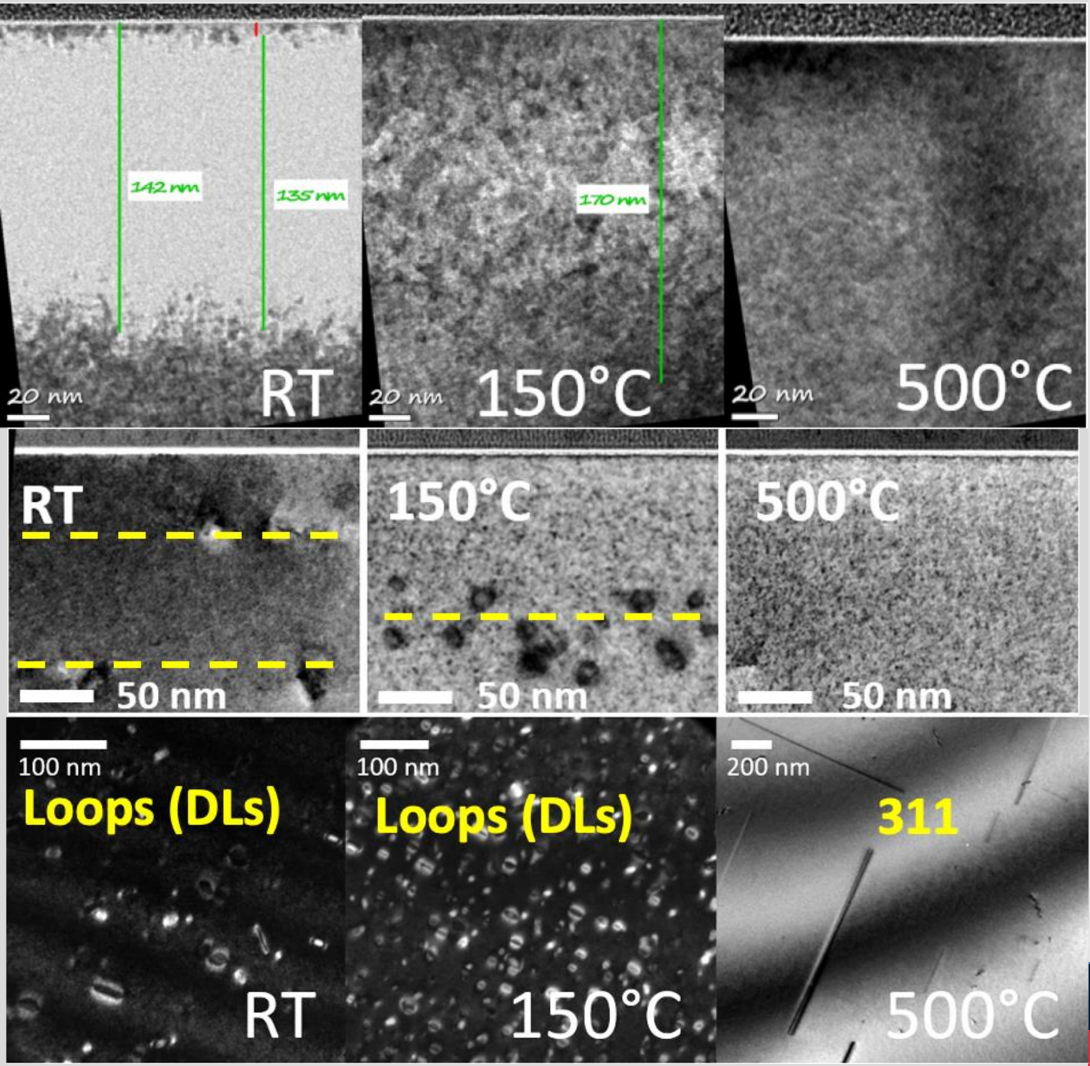
- to optimize manufacturing processes and reduce costs
- to simulate processes and minimize defects

TCAD



Implantation of As in Silicon

EXPERIMENTAL EVIDENCES



TEM as-implanted

- Amorphous layer in RT implant
- No amorphous layer for 150°C and 500°C implants
- Damaged area in 150 °C case

TEM post-annealing

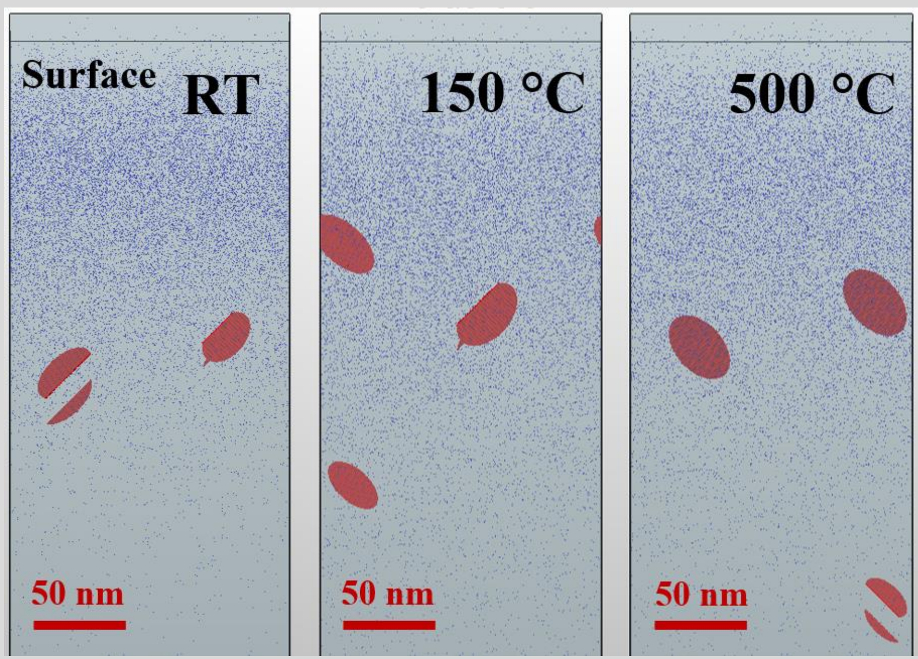
- **Defect location**: Amorphous layer has an impact on the depth of the defects
- **Defect type**: Dislocation loops (DLs) in RT and 150°C / {311} defects in 500°C case
- **Defect density**: More interstitials trapped in RT and 150°C than in the 500°C

I in DLs	
RT	150°C
1.4 10^{14} cm^{-2}	1.6 10^{14} cm^{-2}

I in {311}
500 °C
5.4 10^{12} cm^{-2}

Implantation of As in Silicon

Modeling – KMC default calibration



KMC post-annealing

Defect type:

- **RT**: DLs simulated **agree with TEM**
- **150°C**: DLs simulated **agree with TEM**
- **500°C**: DLs simulated **different from {311} in TEM**

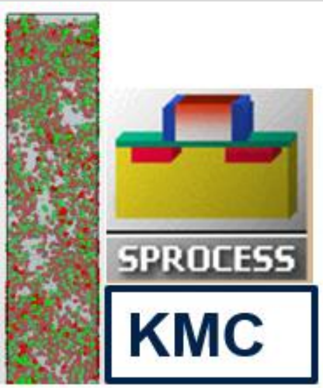
Defect density

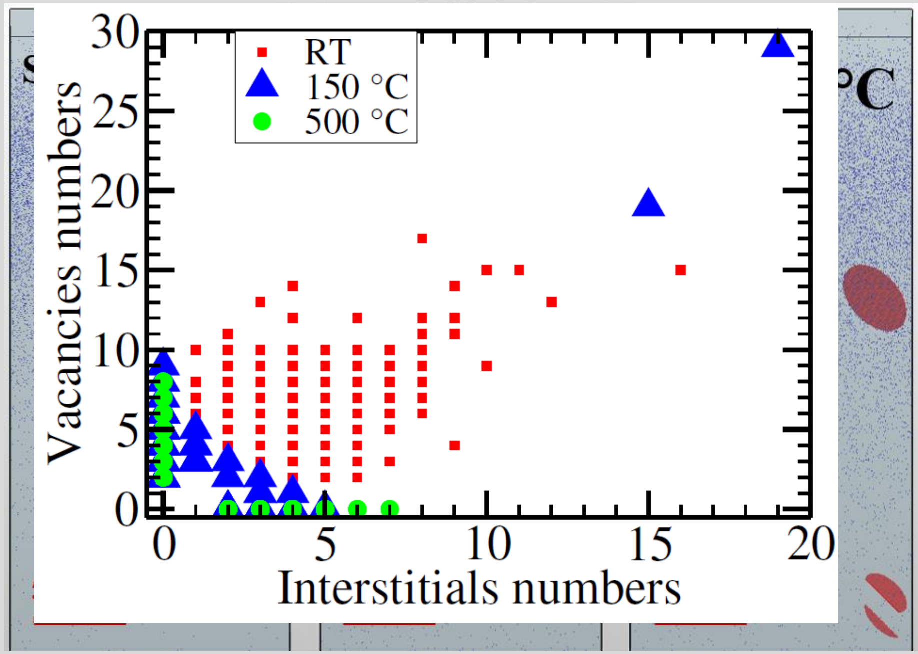
	RT	150°C	500°C
TEM	1.4 10^{14} cm^{-2}	1.6 10^{14} cm^{-2}	5.1 10^{12} cm^{-2}
KMC	1.4 10^{14} cm^{-2}	2.4 10^{14} cm^{-2}	1.9 10^{14} cm^{-2}
	✔	✔	X

KMC simulations are accurate for RT and 150°C cases but not for 500°C implants

Implantation of As in Silicon

Modeling – KMC default calibration





What parameter to change?

- Same annealing sequence after the implants
  → **The difference should be observed in the as-implanted state of the material**

- What are the defects produced by a single As atom implanted?

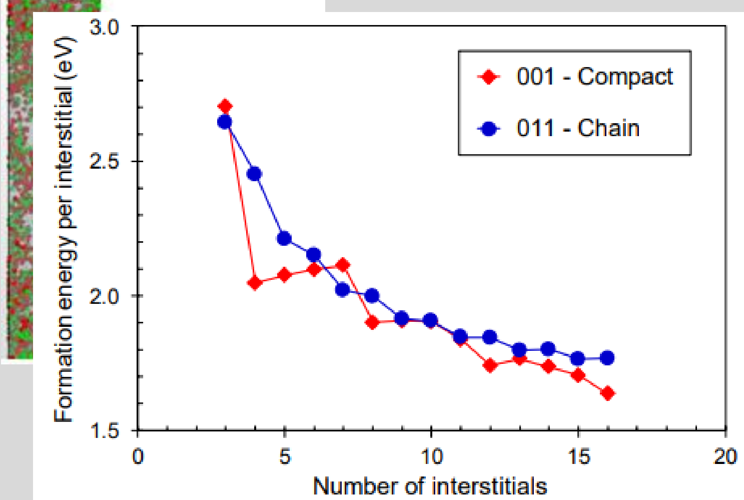
In 500°C SMIC with size < 7

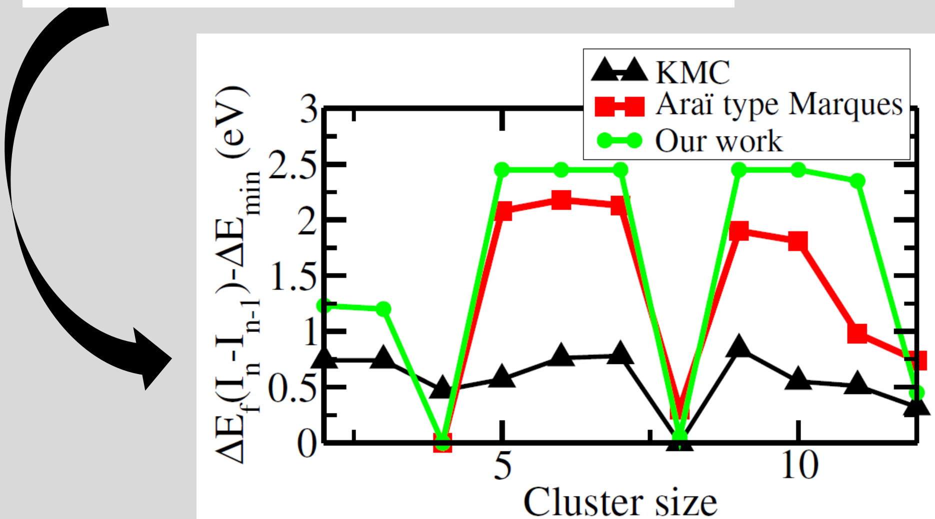
Calibration of small interstitial clusters (SMICs) is required

Histogram of interstitials-vacancies defects for an As atom implanted at RT, 150°C and 500°C

Implantation of As in Silicon

Modeling – KMC – New calibration from atomistic data



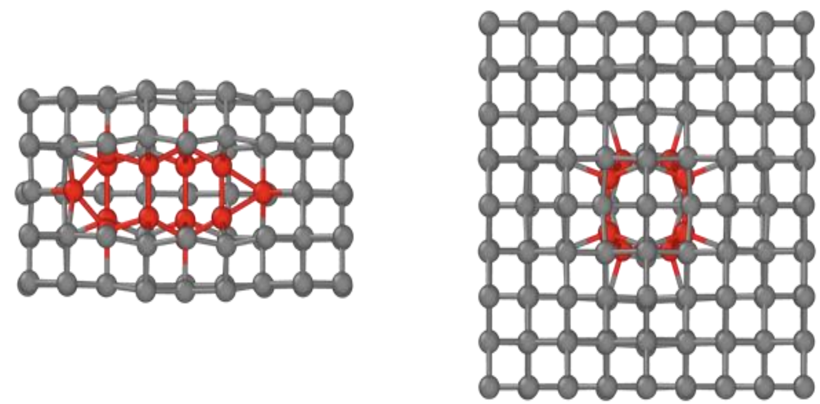


What are the SMIC energies in literature ?

- Two SMIC types in literature :

Chain-like and Araï like (001-Compact)

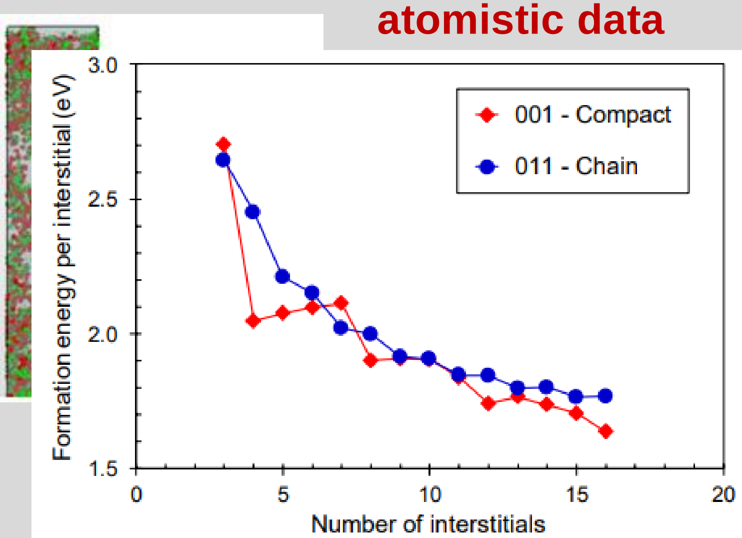
Ref. MD simulation - Marques (2019). Acta Mater. 166, 192-201

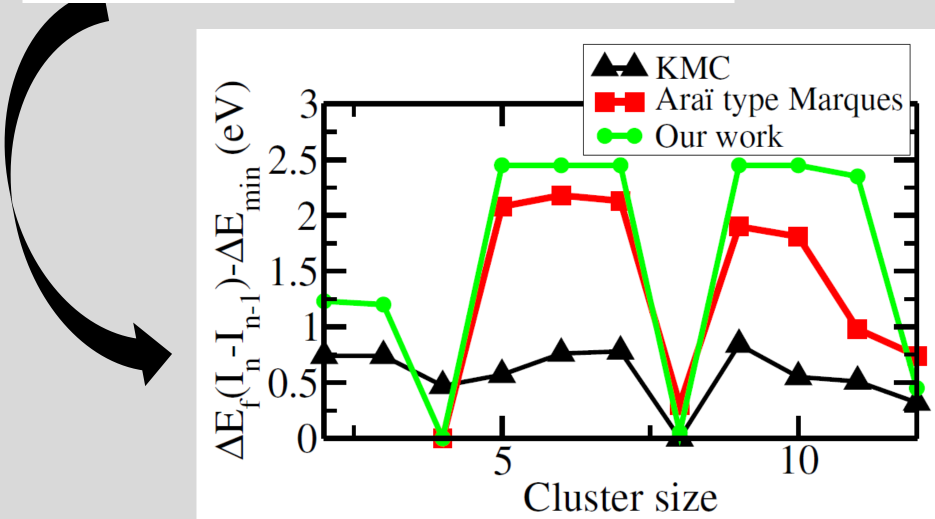


SMIC of Araï type should be considered in detail

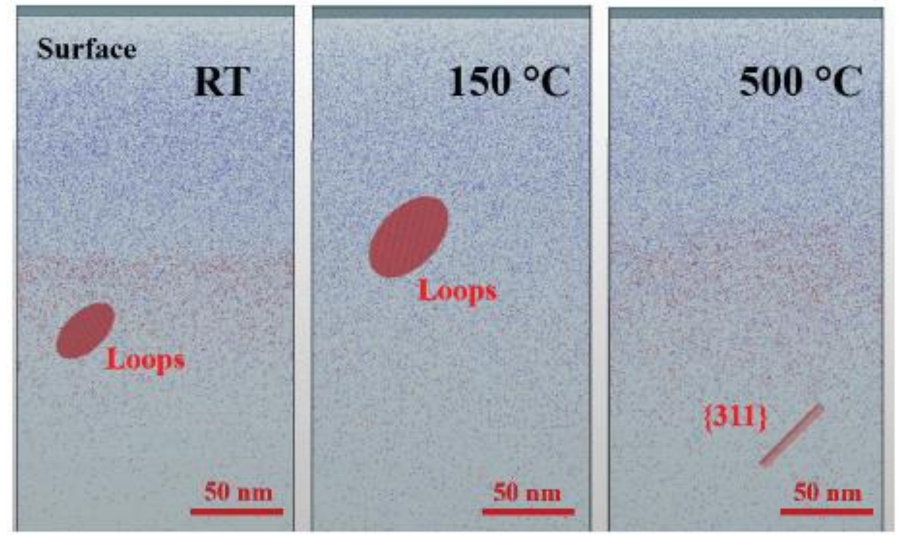
Implantation of As in Silicon

Modeling – KMC – New calibration from atomistic data





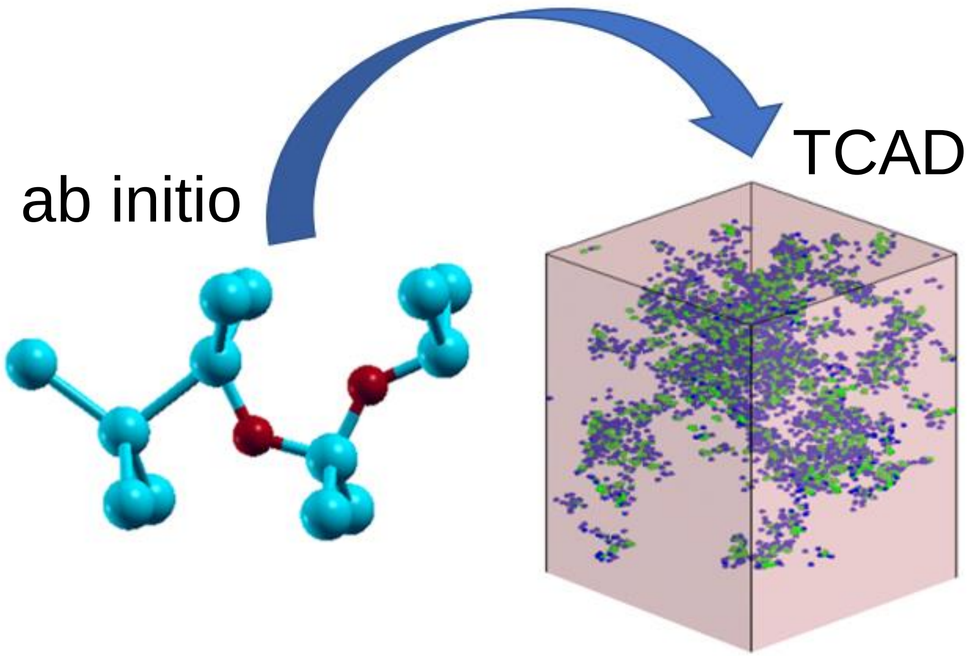
What if the MD trend for Araï SMICs energies is used to fit experiments?

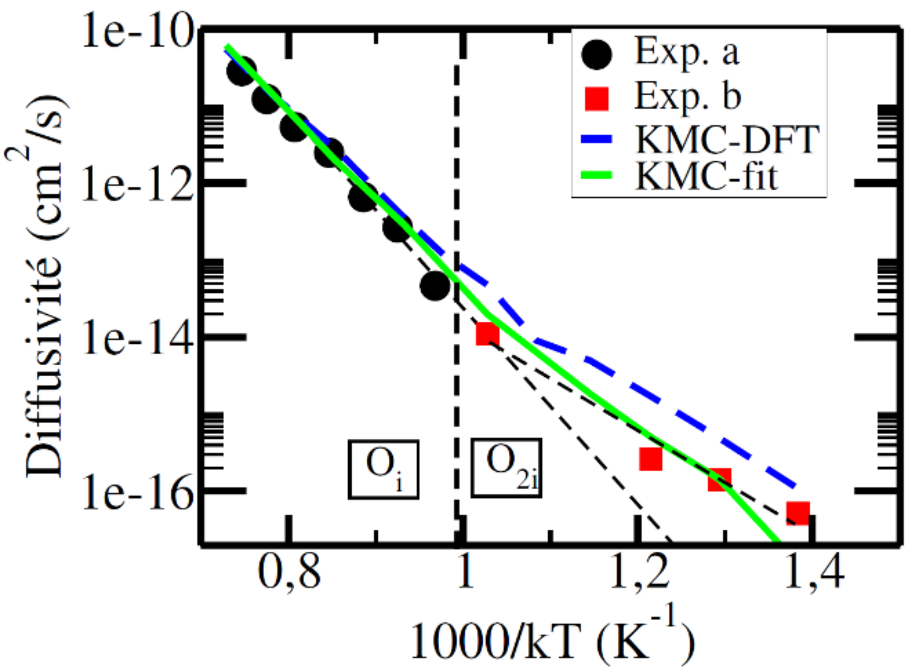


Reproduce the extended defects trends for the 3 implantations

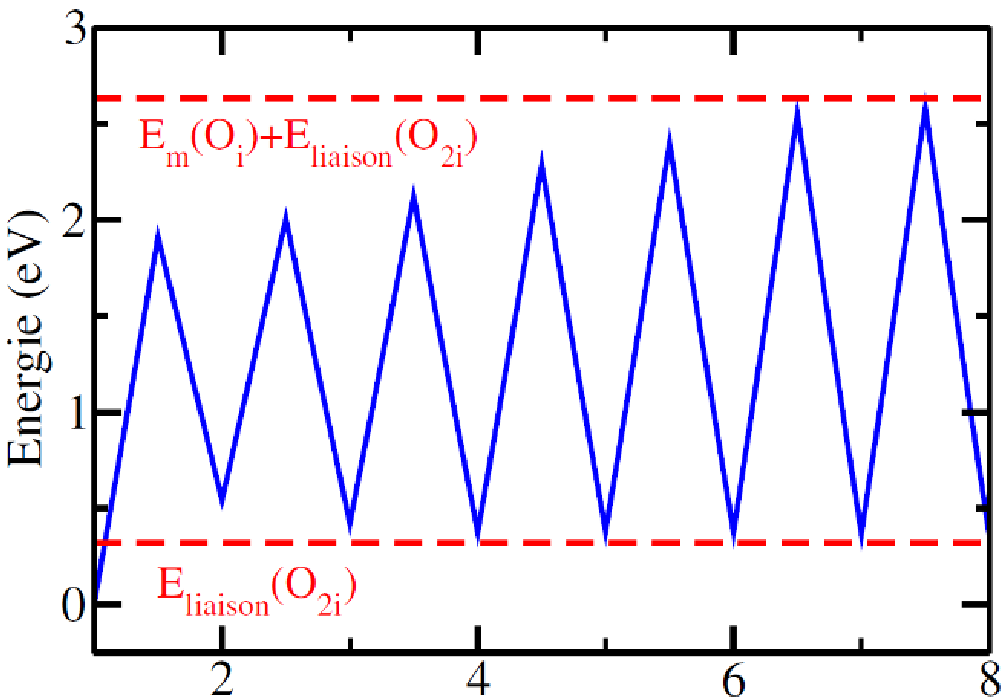
➢ **Need for fine atomistic ingredient in TCAD**

O diffusion in Si

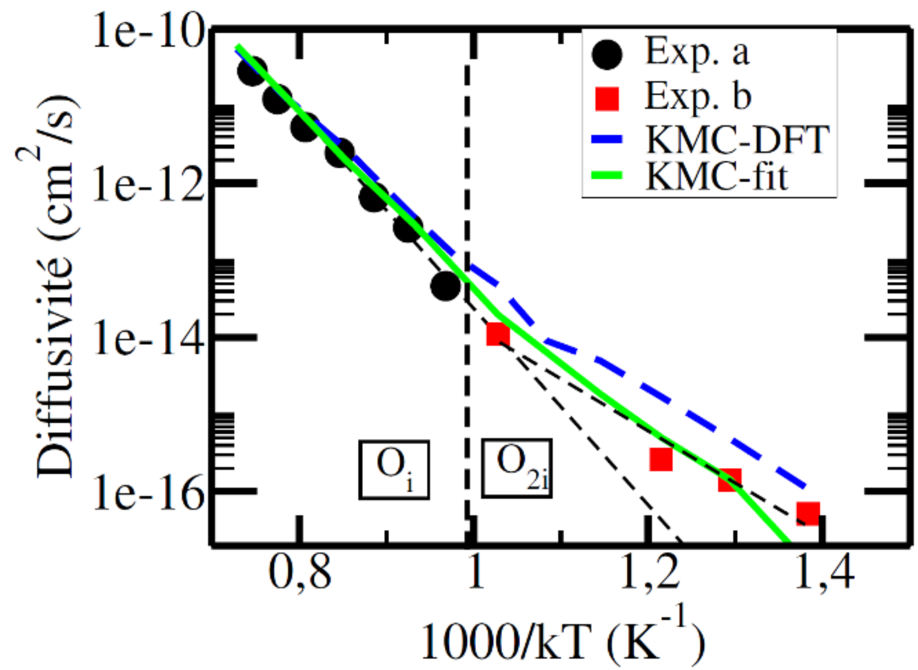




O diffusion in Si



Number of Si atoms separating the 2 O atoms



➢ **Need for ACCURATE atomistic ingredient in TCAD**

- KMC simulates evolution of a system by propagating **chosen relevant events** from a catalog of events, according to **their probability**
  - Large number of minima on the PES, huge number of paths connecting them

Rate of the event Probability

- KMC assigns a **residence time** associated with each state of the system. This temporal evolution is determined by the time until the next event is expected to occur.

Choice of event

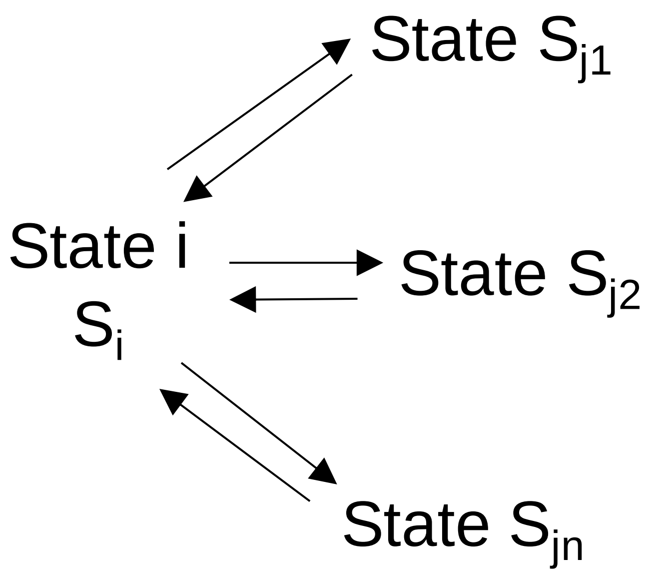
- **State to state dynamics:** The system stays in a given configuration for a long time to get *uncorrelated jumps*. **Jumps are memoryless**, *i.e.* what is likely to happen next only depends on the current state of the system, and not on how this state was reached.

  → definition of a Markov walk that propagates the system from a state to state

Temporal evolution

Master Equation

This is the differential equation describing the temporal evolution of a system. It is a rate equation for the states of the system.



ESCAPE

The time variation of the probability of being in a given state is influenced by the transition rates to and from that state.

$$\frac{dP(Si,t)}{dt} = \sum_{j \neq i} \left(k(S_j - Si)P(S_j,t) - k(S_i - Sj)P(S_i,t) \right)$$

Detailed balance gives relations between forward and reverse probabilities

$$k(S_j - Sj)\ P(S_j,t) = k(S_i - Sj)P(S_i,t)$$

- Said to be reversible or to satisfy detailed balance
- Equilibrium of the system

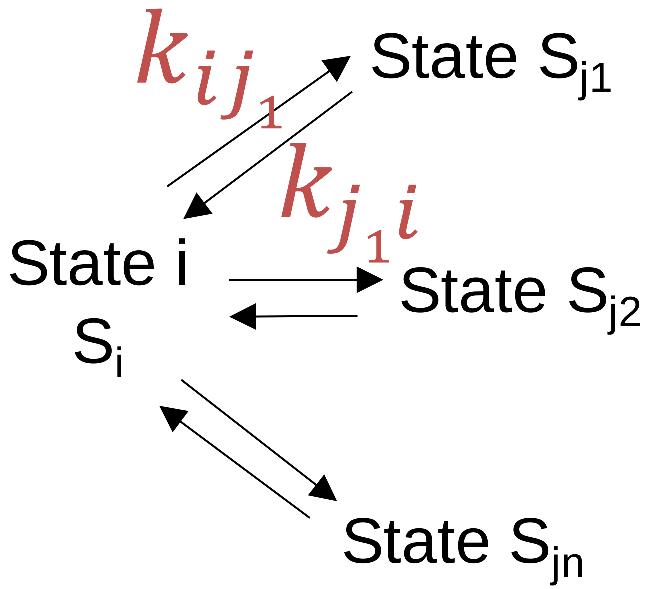
Consider both the reaction from $S_i \rightarrow S_j$ and $S_j \rightarrow S_i$

- **Rate of the event Probability**

k_{ij} Rate constant that defines the probability per unit time = time that the reaction takes to occur (independent from what step preceded state i)

Often described by

$$P \; \alpha \; \exp(-E_b/kT)$$



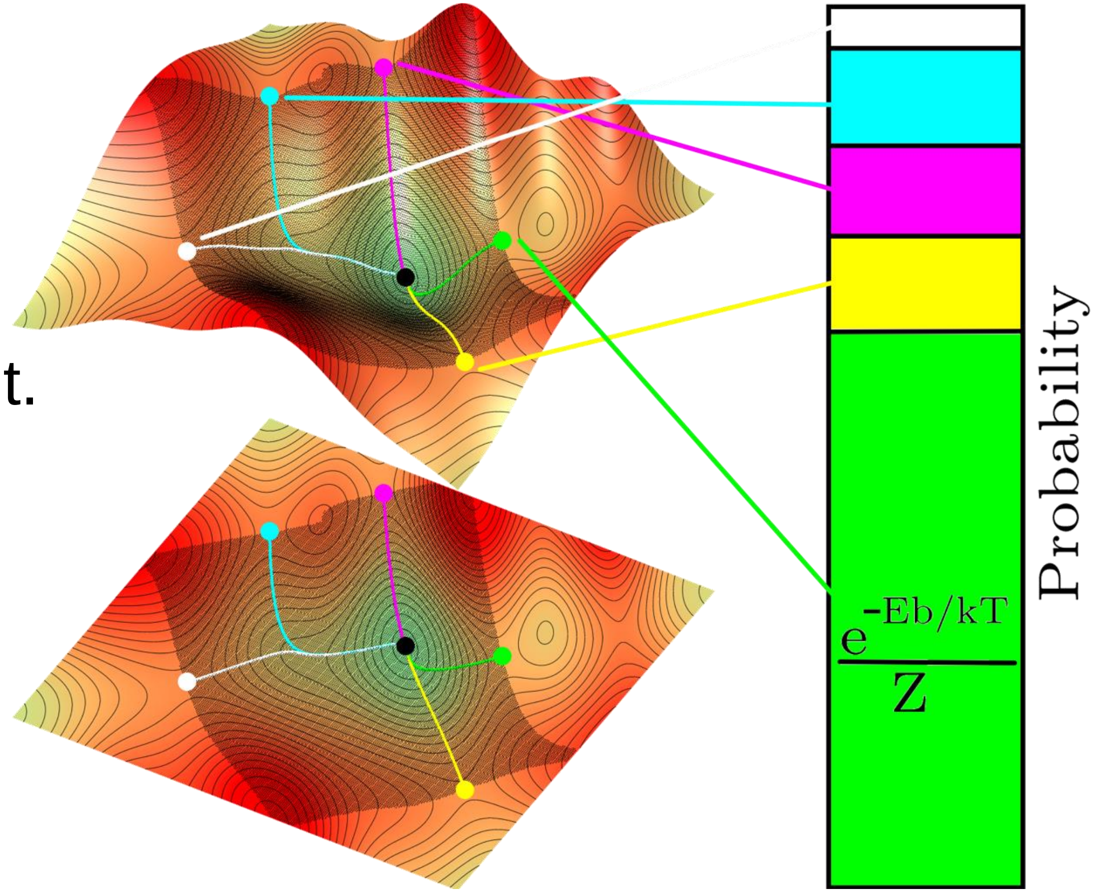
ESCAPE

For accurate simulation, we need to know all the rate constants of all the events for every state we enter.
The rates must be known in advance, the KMC algorithm simply uses them.

- **Choice of event**

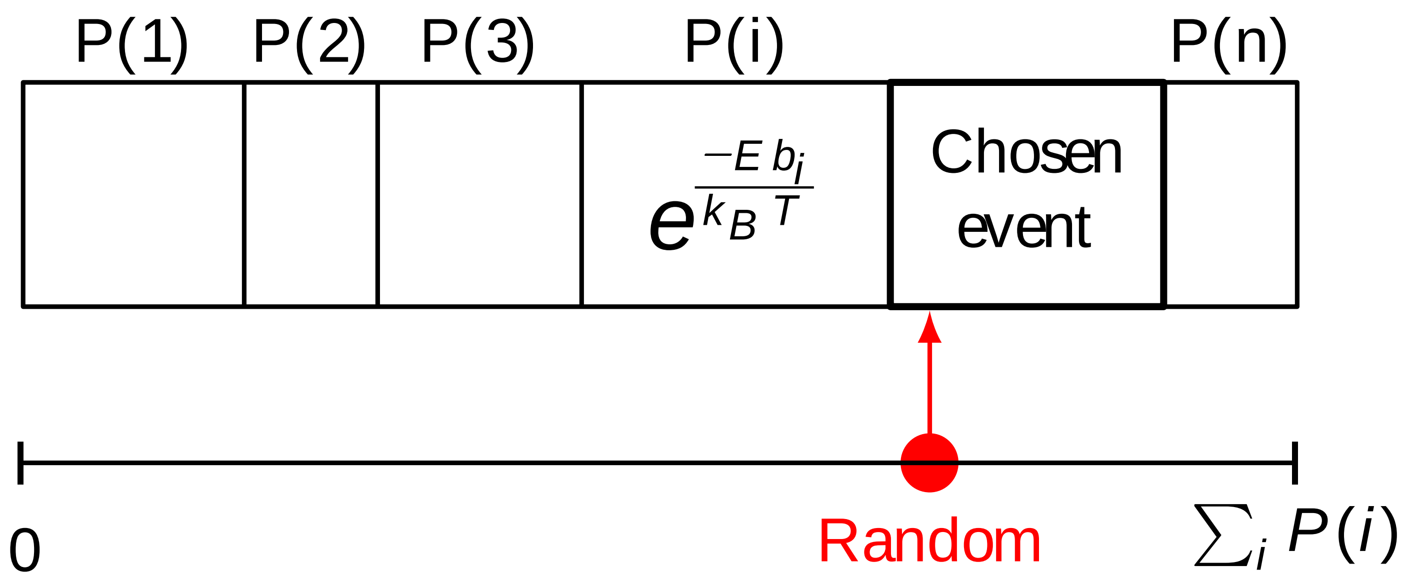
For one given configuration, the system has many possibilities to jump from one configuration to the other.

For each of the possible events, probability distribution is determined and tabulated based on the weight of the rate constant.

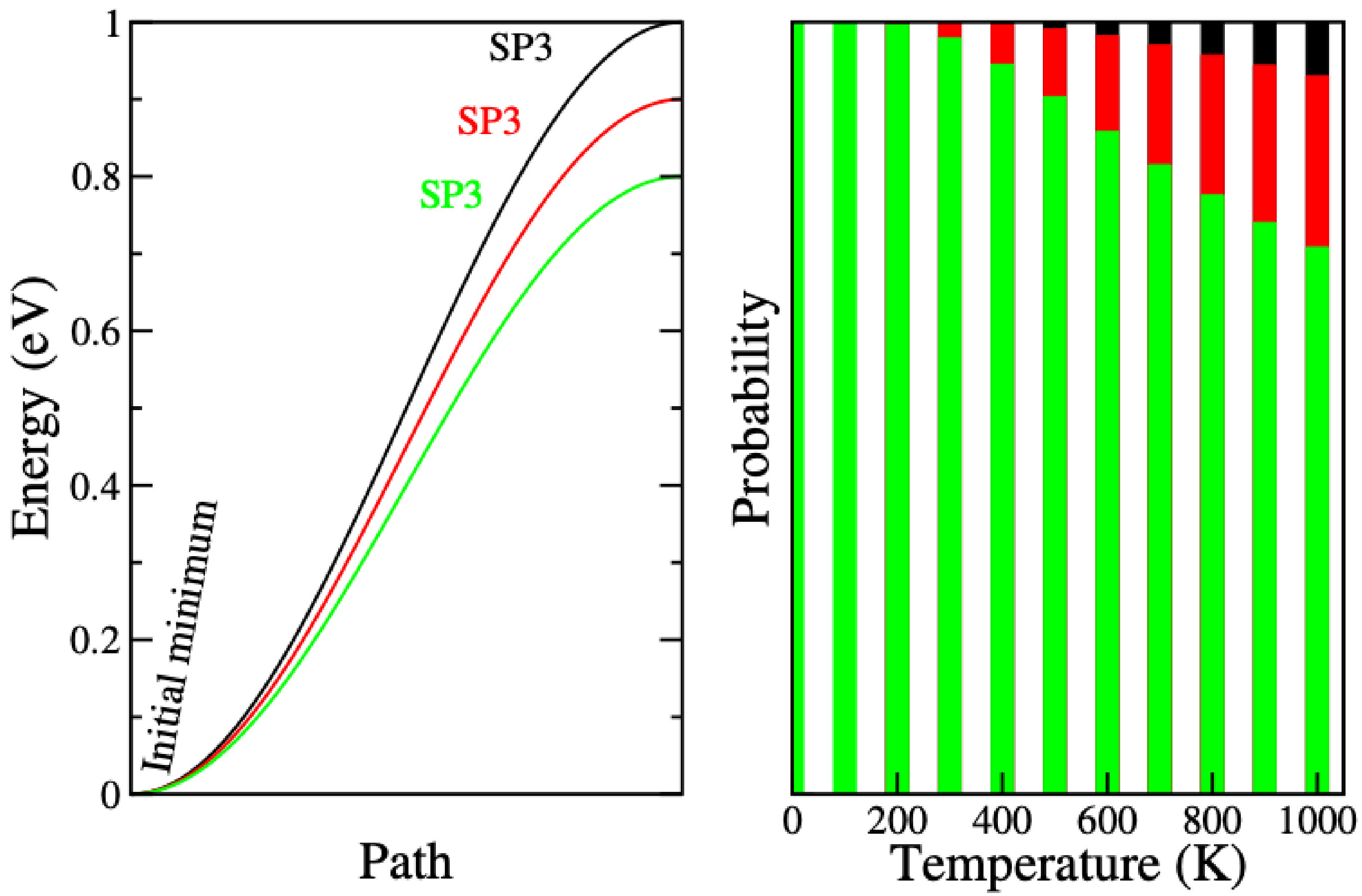


- Choice of event

Random selection of the event: a random number is used [0,1]



- Choice of event



- Temporal evolution

Continuous Time: KMC uses a stochastic clock to advance time continuously according to the transition rates of different events: t = t + Δt

Increment time Δt: Escape depends only on the rate constants. During each increment time, it has the same probability to find an escape path as it had in the previous increment time.
The time between jumps is exponentially distributed, with a characteristic decay time

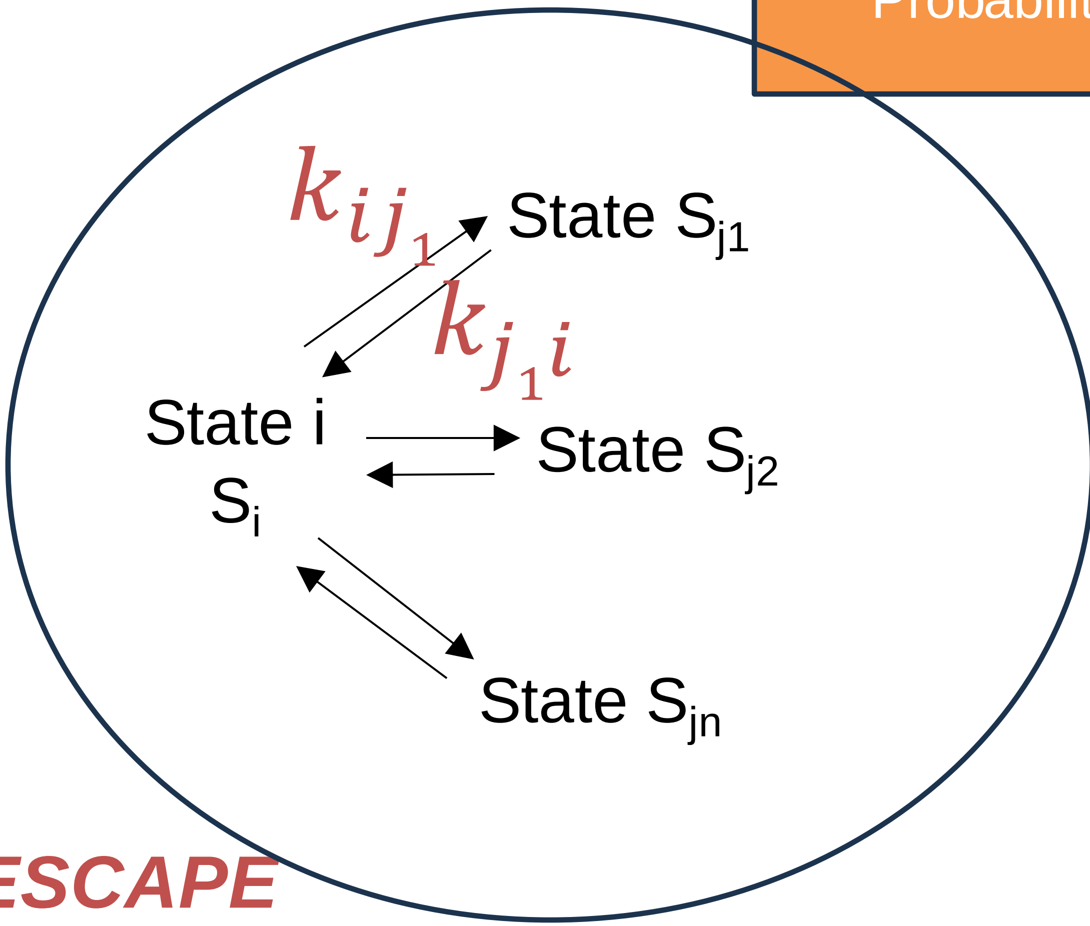
$$\tau = \frac{1}{\sum_j k_{ij}} \text{ (from i to j)}$$

As we introduce stochastic process, a random number [0,1] is added

$$\tau = \frac{-\ln(n)}{\sum_j k_{ij}} \qquad \tau = \Delta t$$

➢ KMC STEP

Rate of the event
Probability



ESCAPE

$\sum_j k_{ij}$

Partition Function
- Weighted probability
- Increment time
- Stochastic

Stochastic choice of event

Temporal evolution

➢ System update

5. KINETIC MONTE CARLO ALGORITHMS

```
procedure KMC( event_catalogue )
    while continue_simulation do
        IDENTIFY_POSSIBLE_EVENTS()
        CHOOSE_EVENT()
        APPLY_EVENT()
        UPDATE_SYSTEM()
    end while
end procedure
```

Standard algorithm / rejection

Step 0 - Set the time t = 0, initial configuration

Step 1 - Form a list of all the rates k_{ij} of all possible transitions P_i in the system

Step 2 - Calculate the partition function where N is the total number of transitions.

$$Z = \sum_j k_{ij} \qquad for\ i = 1, \ldots, N$$

Step 3 - Choose a transition at random $S_i \rightarrow S_j$

Step 4 - Get a random number $n \in [0, 1]$

Apply event if $n < \frac{k_{ij}}{Z}$

Step 5 - If transition accepted, pick a random number $n \in [0, 1]$, and increase time

Otherwise the event is rejected

→ Return to step 1

Rate of the event Probability

Stochastic choice of event

Temporal evolution

➢ (Bortz, Kalos and Lebowitz) BKL algorithm

Step 0 - Set the time t = 0, initial configuration

Step 1 - Form a list of all the rates k_{ij} *of all possible transitions* P_i *in the system*

Step 2 - Calculate the partition function $Z = \sum_j k_{ij}$ *for i = 1,…, N where N is the total number of transitions.*

Step 3 - Get a uniform random number n ∈ [0, 1]

Step 4 - Find the event to carry out i by finding the i for which

$$P(i_k) < n < P(im)$$

Step 5 - Apply event $_i$*, change the local atomic configuration*

Step 6 - Find all P_i *and recalculate all* k_{ij} *which may have changed due to the transition*

Step 7 - Get a new uniform random number n ∈ [0, 1]

Step 8 - Update the time

→ *Return to step 1*

Rate of the event Probability

Stochastic choice of event

Temporal evolution

First reaction method

Step 0 - Set the time t = 0, initial configuration

Step 1 - Form a list of all the rates k_{ij} of all possible transitions P_i in the system

Step 3 - For each possible event $S_i \rightarrow S_j$, get a random number n ∈ [0, 1] and compute associated time

$$\tau = \frac{-\ln(n)}{k_{ij}}$$

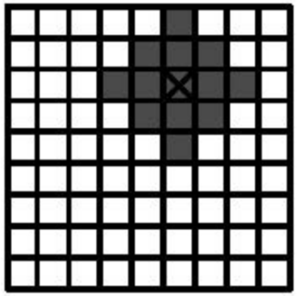
Step 4 - Select the event $S_i \rightarrow S_j$ with the lowest τ

Step 5 - Apply selected transition, and increase time by τ .

Step 6 - Return to step 1

(advantage: previous computations are stored, only nearest neighbors and associated events are updated)

→ Return to step 1



Rate of the event Probability

Stochastic choice of event

Temporal evolution

List of events

Known in advance: KMC only uses events
Assumption that **events are well defined and that their transition rates** are constant or can be calculated

However, in complex systems, events may be dependent on the environment and local conditions, making them difficult to describe. Same for long range interaction.

Limits:
Calculation of Rates: The accuracy of KMC is highly dependent on the accuracy of transition rates. Calculating these rates accurately can be difficult, especially for complex systems.

Modelling error: Incorrect transition rates can lead to bad results, reducing the reliability of simulations.

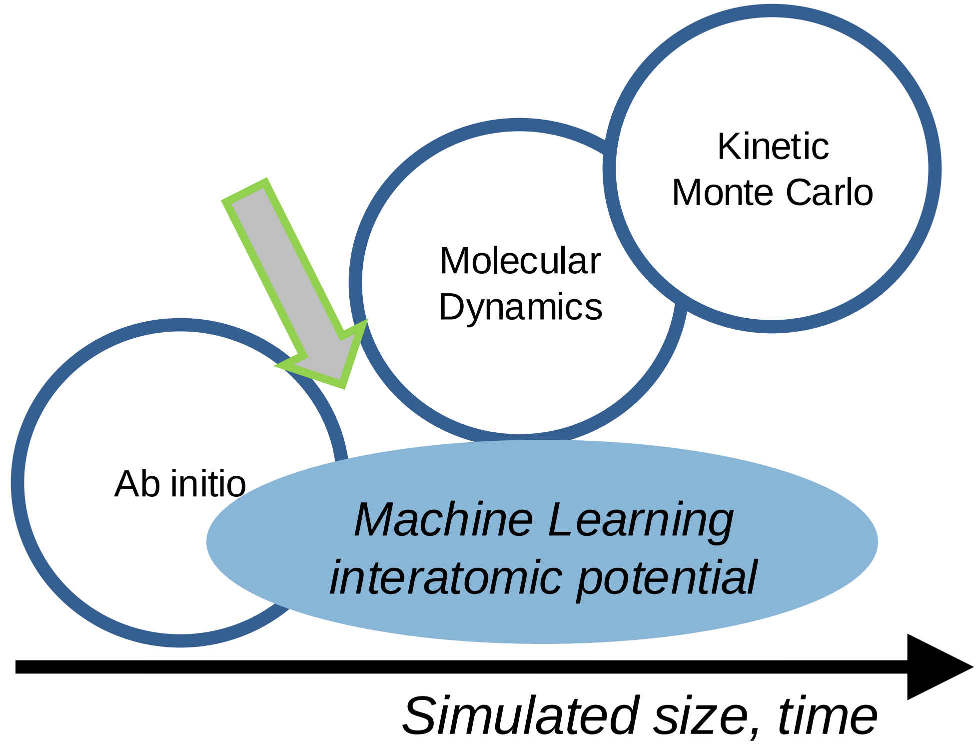
Model accuracy: The importance of accuracy in transition rate models for reliable results.

6. KINETIC MONTE CARLO

ADDITIONAL COMMENTS

- On the fly kinetic Monte Carlo / Adaptive KMC (AKMC)

- Reconstructing the catalogue on the fly
  - DFT
  - MD
  - ML potential to improve the estimation of transition rates and explore the state space more efficiently



Benefits:

Improves the accuracy of transition rates and reaction paths.

Accelerates state space exploration.

Drawbacks:

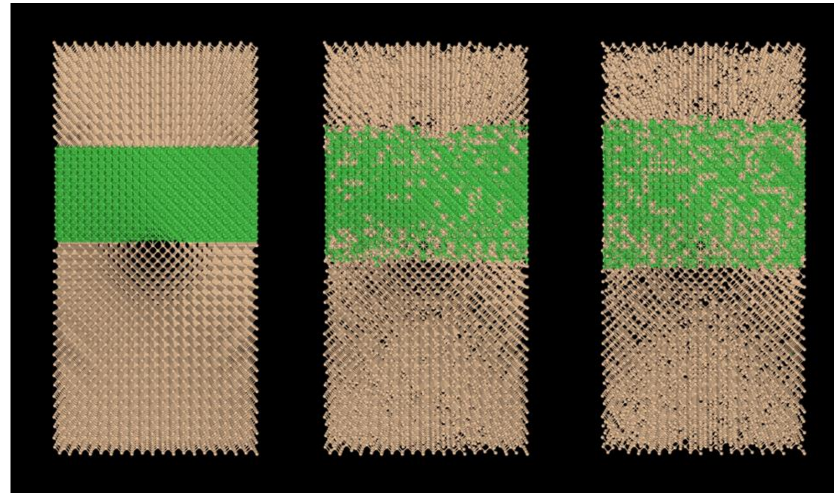
Frequent update of the catalog, computational cost increase

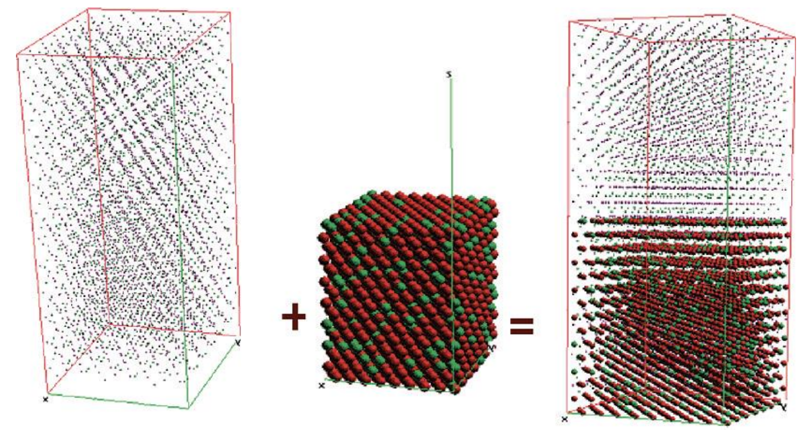
On lattice KMC

- Used to model discretised systems on a grid, such as the growth of thin films, diffusion on surfaces, and other surface phenomena

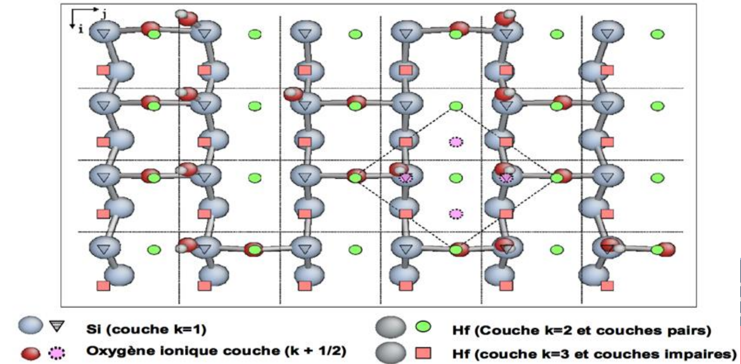
- Define the grid: The grid structure (« lattice ») represents the discrete positions where the atoms are

- Advantages:
  - Simplicity: Easier to implement for systems on grids
  - Efficiency: Suitable for phenomena such as diffusion or surface growth.





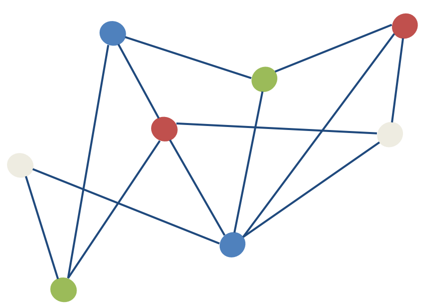
Virtual oxide lattice | Alloy lattice | Alloy embedded in the virtual oxide lattice



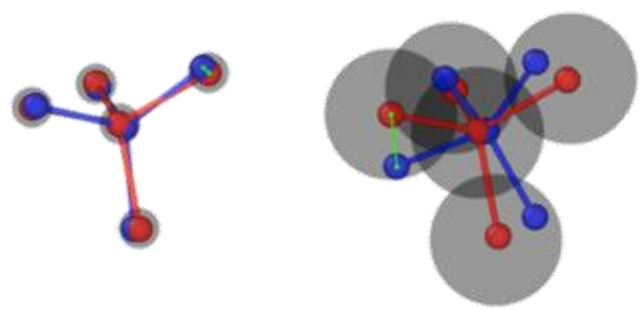
Off lattice KMC (example: kinetic ART)

- The possible topological configurations, all within a continuous space where the positions of entities are not constrained to a fixed lattice.
- **Identification of distinct configurations**: Each possible configuration of the system must be identified based on its topology, and the transitions between these configurations need to be determined.

Representing the position of atoms using graphs



Comparison, matching and shape association descriptor
Identify and compare structures, apply events



Example: IRA-SOFI

Journal of Chemical Information and Modeling **61** (2021) 11, pp. 5446–5457 - doi : 10.1021/acs.jcim.1c00567

Software Impacts **12** (2022) 100264 - doi: https://doi.org/10.1016/j.simpa.2022.100264

Journal of Chemical Physics **161** (2024) 062503 - doi: https://doi.org/10.1063/5.0215689

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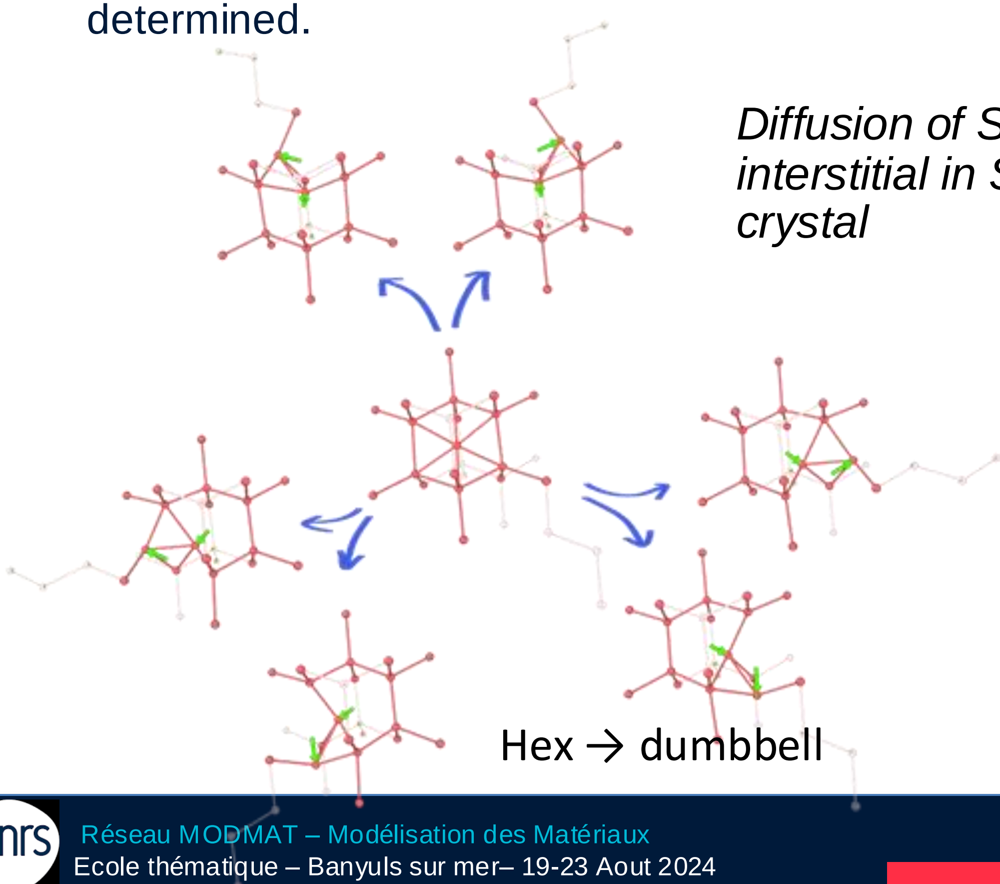


Diffusion of Si interstitial in Si crystal

Co-existing slow and fast transitions

- Multiple Energy Barriers with different heights makes the simulation more complex
- Consequence:
  - Trapping in Local Minima: The system can become trapped in local minima, requiring additional techniques to escape these states.

- Limit :
  - KMC is effective for simulating rare events and slow transitions, but it can be ineffective for systems where there is a wide range of transition times, including coexisting very fast and very slow transitions.

- Consequence:
  - Shifted Timescales: The simulation can become extremely time consuming if it has to resolve very frequent events in addition to rare events.

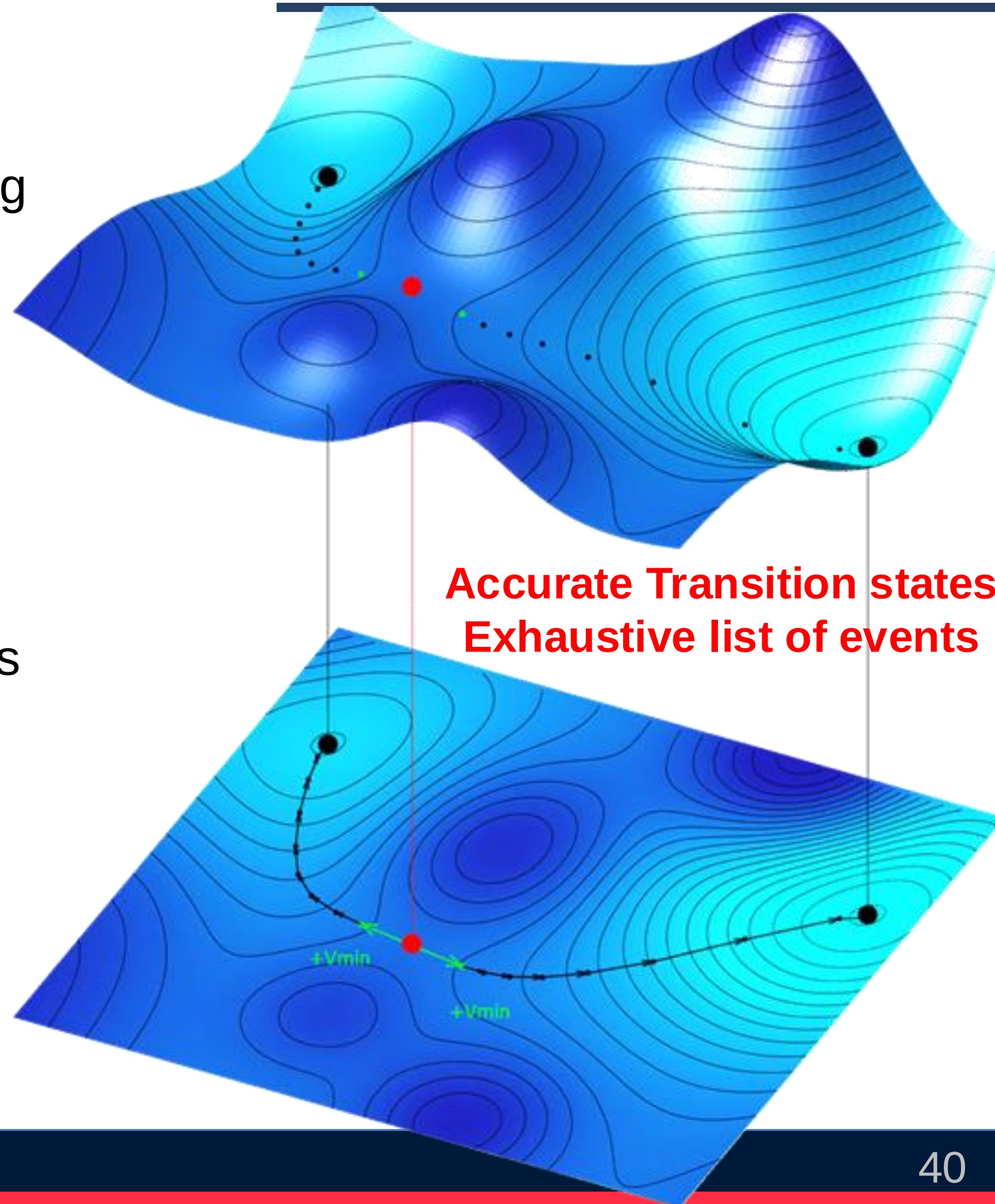
Use the **basin method** to treat transitions between metastable states, avoiding the details of rapid intra-basin transitions.

Temporal accuracy: Accurate modelling of the temporal evolution of systems.

Flexibility / versatile: Applicable to a wide range of dynamic systems, from chemical reactions to diffusion phenomena.

Efficiency: Can simulate rare processes and events on different time scales.

Stochastic: Capable of capturing the fluctuations and random nature of dynamic processes.



Finding Saddle Points on Potential Energy Surfaces:

Exploration with ART

Antoine Jay[1], Nicolas Salles[3],
Miha Gunde[1], Matic Poberznik[3], Layla Martin-Samos[3],
Nicolas Richard[4], Stefano De Gironcoli[3], Anne Hémeryck[1],
Normand Mousseau[5]

[1]LAAS-CNRS, *Université de Toulouse, CNRS, Toulouse, France*
[2]CIMI-DEOS, *ISAE Supaéro, Toulouse, France*
[3]CNR-IOM, *Democritos and Sissa, Trieste, Italy*
[4]CEA, DAM, DIF, *Arpajon, France*
[5]Université de Montréal, *Montréal, Canada*

Overview

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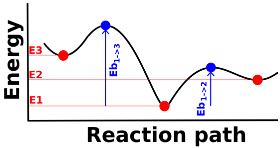
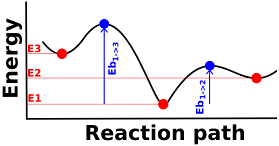
Goal

From an atomic structure, discover new structures and energy barriers



Goal

From an atomic structure, discover new structures and energy barriers



Minima → thermodynamics

$$Prob(i) = \frac{e^{\frac{-E_i}{k_B T}}}{Z}$$

$$Z = \sum_{i}^{N_{configurations}} e^{\frac{-E_i}{k_B T}}$$

Saddle points → kinetics

$$k_{1\rightarrow 2} = \omega_{vib} e^{\frac{-(E_b)}{k_B T}}$$

$$\omega_{vib} = \frac{\prod_i^{3N_{at}} \omega_i(State1)}{\prod_j^{3N_{at}-1} \omega_j(saddle)} \sim 10^{13} Hz$$

$$\Delta t = -\frac{ln\lambda}{\sum_n k_n}$$

Why is it complicated? Blind=local

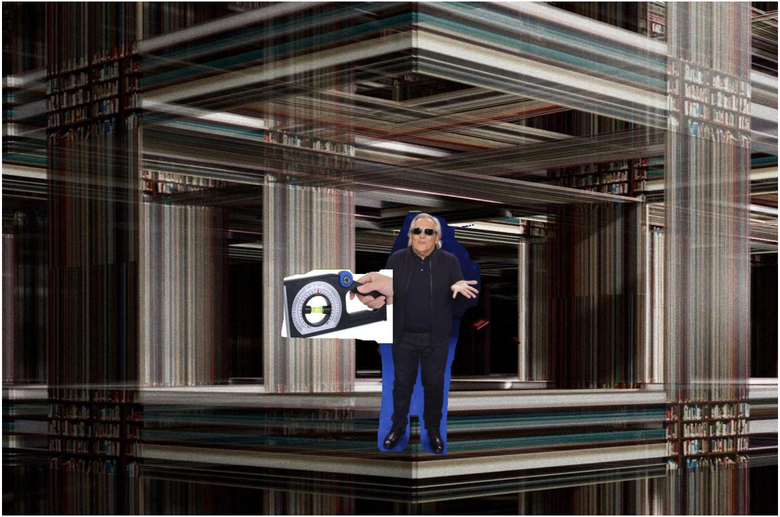
Why is it complicated? Only forces

Why is it complicated? fast

Why is it complicated? efficient

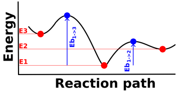
Why is it complicated? efficient

Why is it complicated? N dimensions

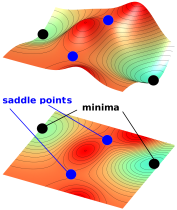


Definitions: Minima and Saddle points

1D



2D

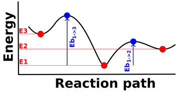


$3\times N_{at}D$

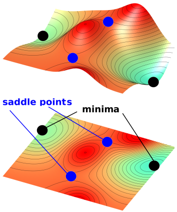
?????

Definitions: Minima and Saddle points

1D



2D



$3 \times N_{at}$D

?????

Minimum:
min in $3N_{at}$ D

Saddle point:
max in 1D,
min in $(3N_{at}-1)$D

Steps:

- Find the vector corresponding to this D
- Minimize in the orthogonal hyperplane.

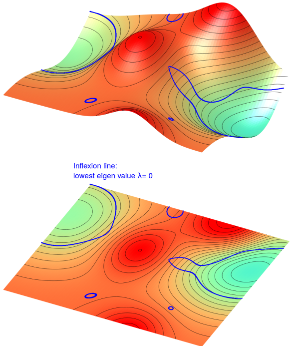
Convergence: $\forall i,\ F_i = \frac{dE}{dx_i} \sim 0$

Definitions: Hessian Matrix and inflexion

$$H_{ij} = \frac{\partial^2 E}{\partial x_i \partial x_j}$$ eigenvalues λ_i and eigenvectors $\mathbf{V_i}$

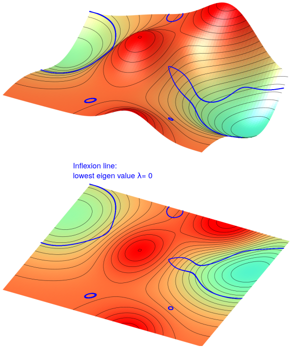
Harmonic bassin: $\forall i, \lambda_i > 0$

Minima: $\frac{\partial E}{\partial x} = 0$



Above Inflexion: $\exists i, \lambda_i < 0$

Saddle points: $\frac{\partial E}{\partial x} = 0$



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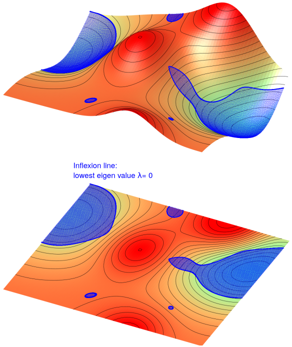

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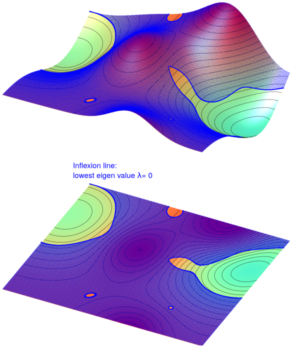
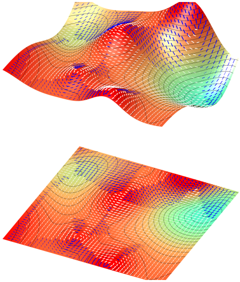


Only the lowest eigenvalue λ_{min} and $\mathbf{V_{min}}$ are needed

$\rightarrow$ LANCZOS

Definitions: Valleys, Forces, Eigen Vectors

Eigen Vectors:
$\mathbf{V_{min}}$ from Hessian



$\rightarrow \parallel$ MEP

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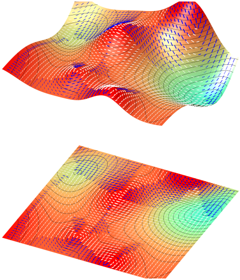
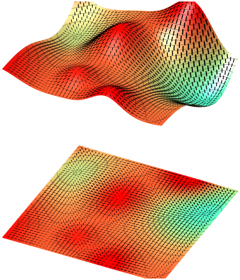


$\rightarrow \parallel$ MEP

Forces:
$-\frac{\partial E}{\partial x}$



$\perp$ isolines

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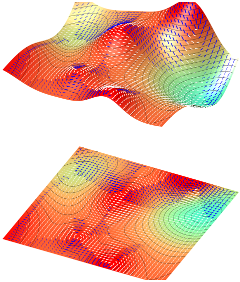

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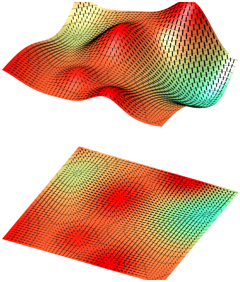
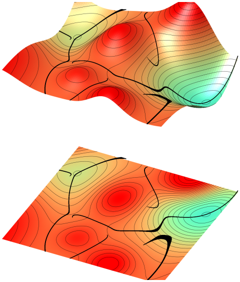


$\perp$ isolines

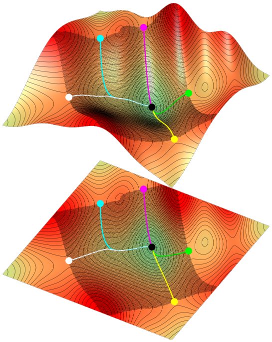
Valleys:
$\mathbf{V_{min}} \parallel \mathbf{F}$ or $\mathbf{F}_\perp = 0$



is MEP

Definitions: Asymetric problem

Basin and IRC



Definitions: Asymetric problem

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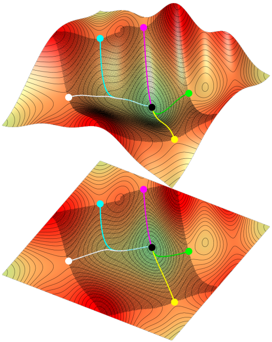
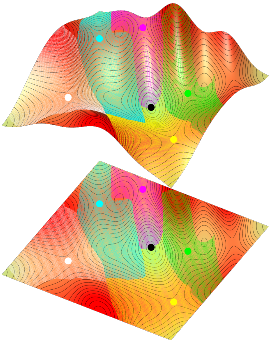
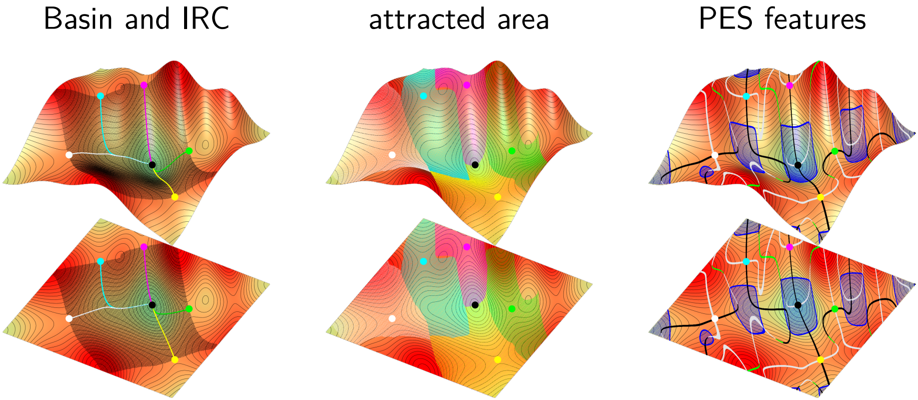


attracted area



Definitions: Asymetric problem



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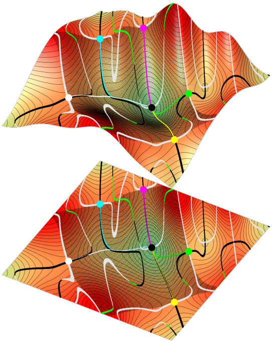

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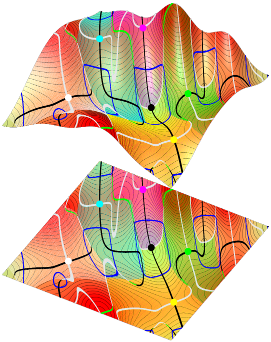
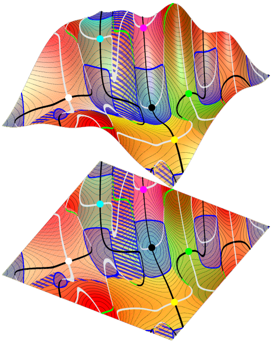


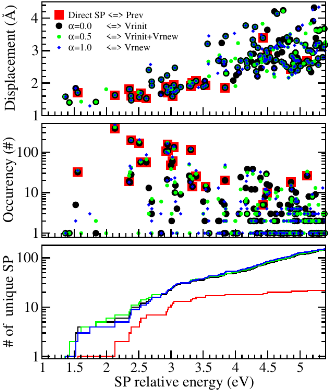
PES features



Definitions: Asymetric problem

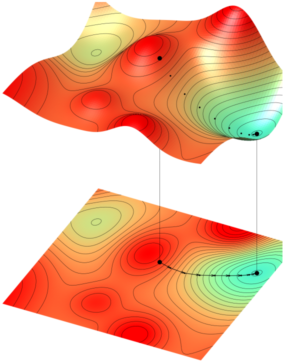
V_{CR}	Prev	V_{min}	Vr_{init}	$Vr_{init} + Vr_{new}$	Vr_{new}
Total SP	712	2793	2967	3000	3000
All CSP	708	2095	2591	2652	2711
Unique CSP	23	127	248	237	225

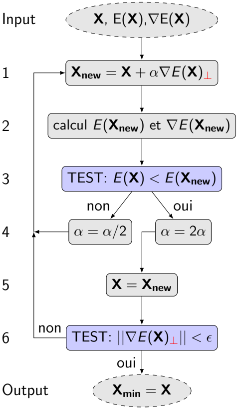
(a) Total number of SPs found with each method. *All CSP*: counting only the connected SP. *Unique CSP*: counting CSPs reached several times only once. *Prev*: previous ARTn approach that stops in CR.



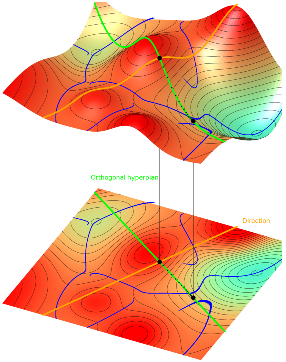
Definitions: Simple Vs Orthogonal relaxation

Simple





Orthogonal



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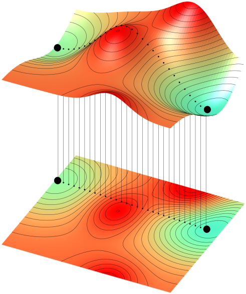
DRAG method: for new minima only

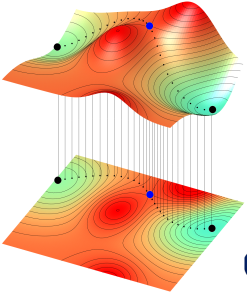
- User gives a direction $\mathbf{D}$
- Loop: $\mathbf{X_{new}} = \mathbf{X_{old}} + \mathbf{D}$; Constrained relaxation;
- Standard minimization if $\Delta E < 0$

Most used method: NEB (1998)

Create a path with intermediate structures (images)
Do until converging:

- define the tangent of the path on each image
- Add a fictive spring force between each image: preserve distances
- Minimize in the hyperplane orthogonal to the tangent





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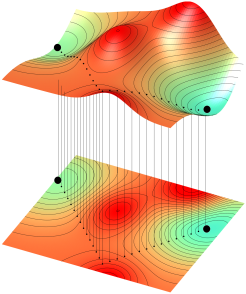
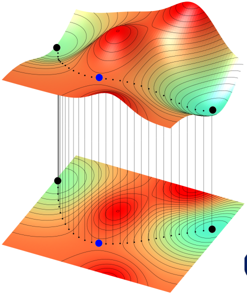
Create a path with intermediate structures (images)
Do until converging:

- define the tangent of the path on each image
- Add a fictive spring force between each image: preserve distances
- Minimize in the hyperplane orthogonal to the tangent





Drawbacks of the NEB

- Need the knowledge of the final structure
  $\rightarrow$ no possible exploration
- Final saddle point depends on the interpolation
  $\rightarrow$ may return false minimum energy path (MEP)
- Convergence depends on the definition of the tangeant
  $\rightarrow$ need high number of images
- Computational cost increases with the number of images
  $\rightarrow$ only the saddle point has a physical meaning
- Saddle point cannot reach low forces
  $\rightarrow$ phonon calculations are less accurate

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Improvement of the NEB

- Climbing image-NEB :
  $\rightarrow$ The Max energy image is allowed to climb
- Auto-NEB :
  $\rightarrow$ Images are added around the max energy image
- Image Dependent Pair Potential :
  $\rightarrow$ The initial path in interpolated respecting distances
- RMI-NEB:
  $\rightarrow$ For symetric paths, the tangent is trivial

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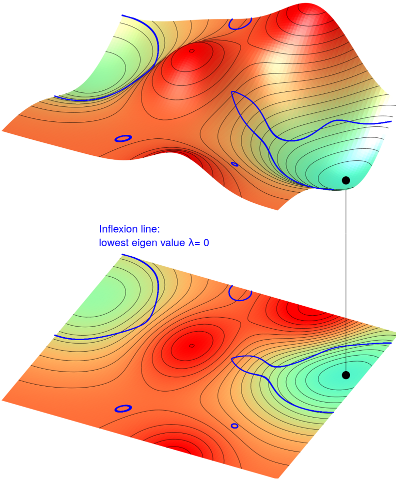
ARTn: Algorithm (1996)

Initial minimum



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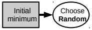

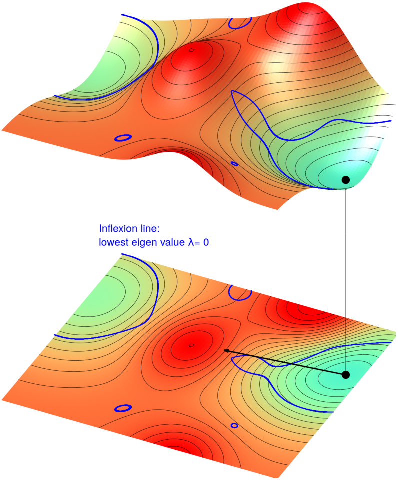

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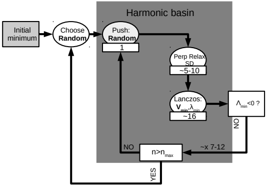
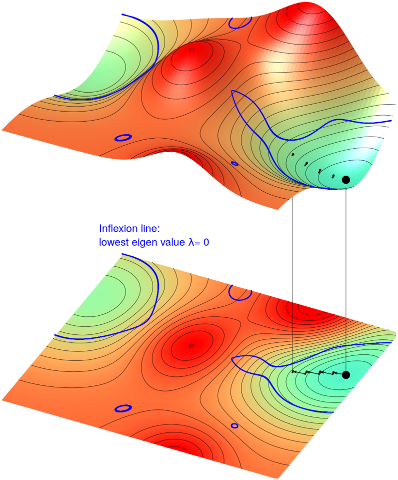
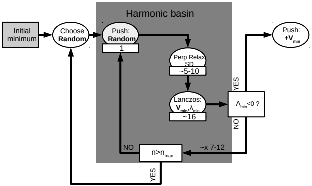
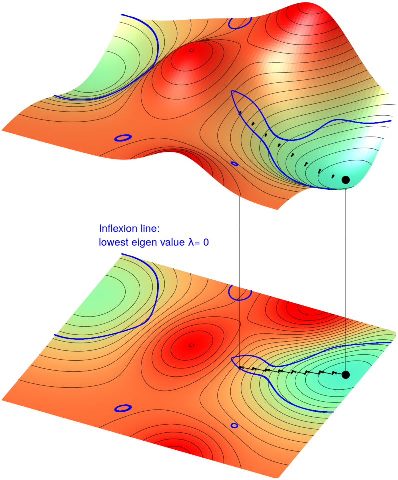




$$||Push|| = cst$$

ARTn: Algorithm (1996)





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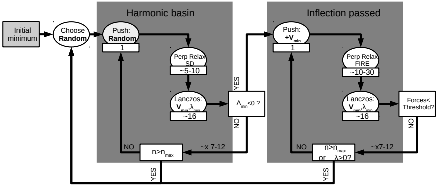
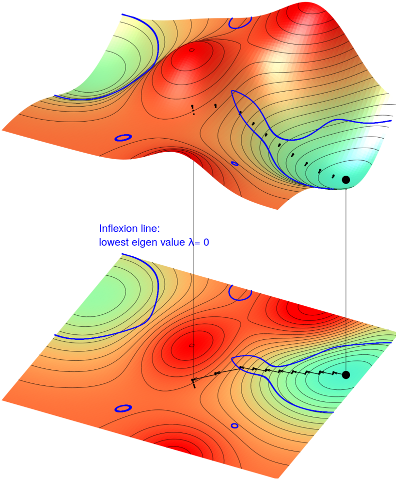


$$||Push|| = min\left(size_{max}, \frac{|f_{par}|}{max(|\lambda_0|, 0.5)}\right)$$



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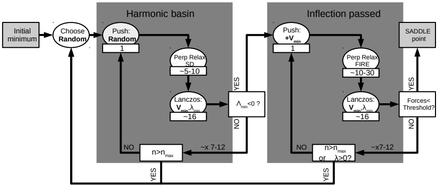

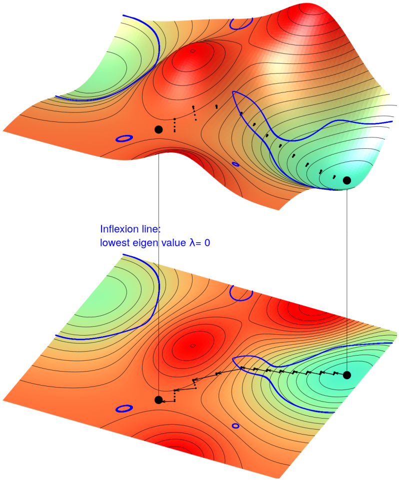

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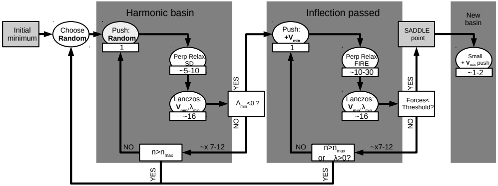
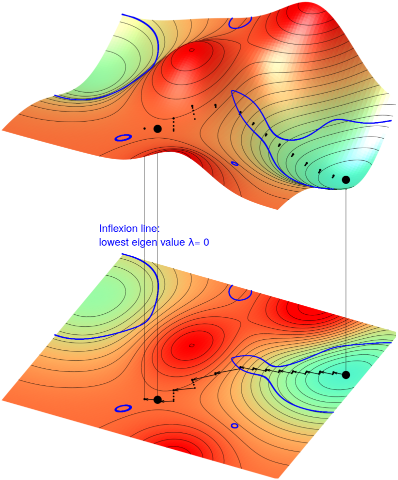
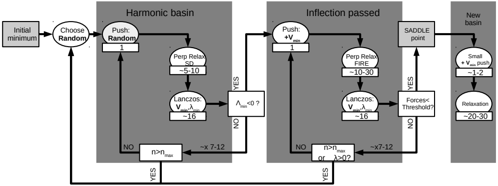
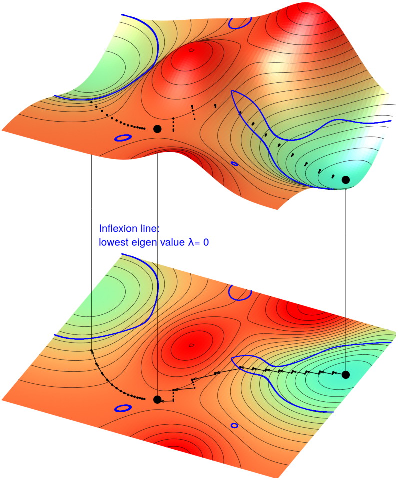




$$||Push|| = 0.1 * (init - saddle)$$

ARTn: Algorithm (1996)





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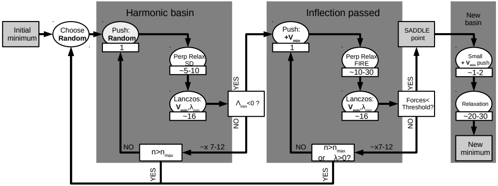

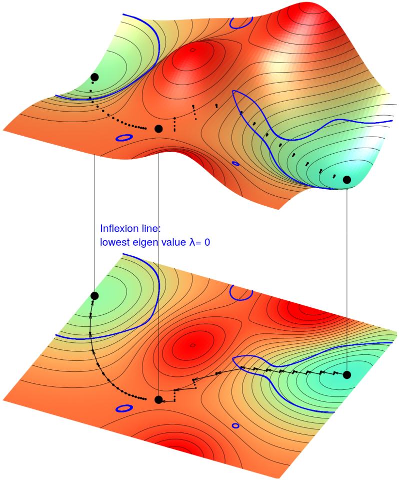

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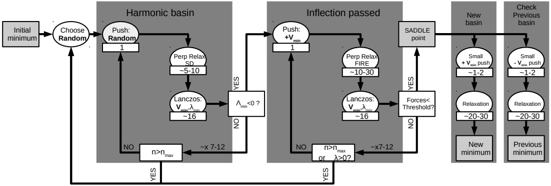

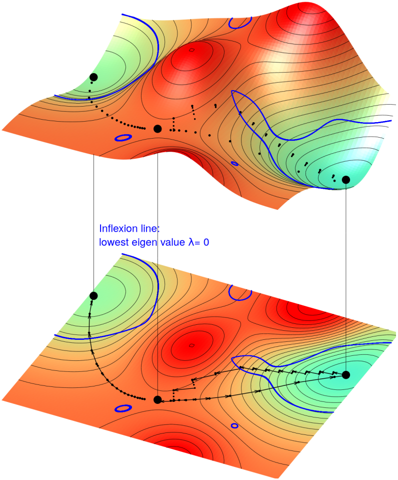

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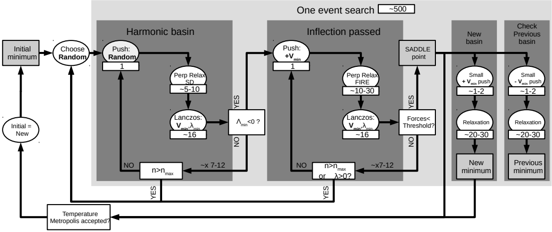

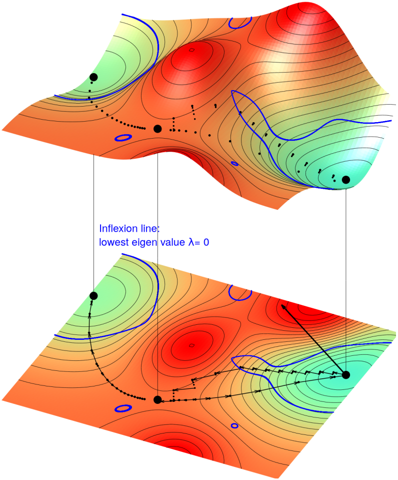

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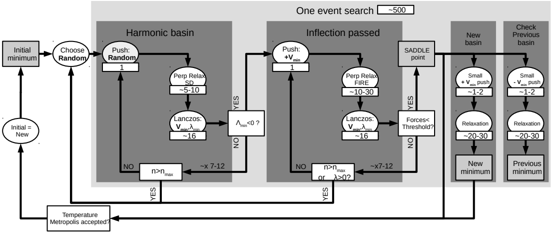
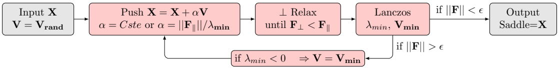
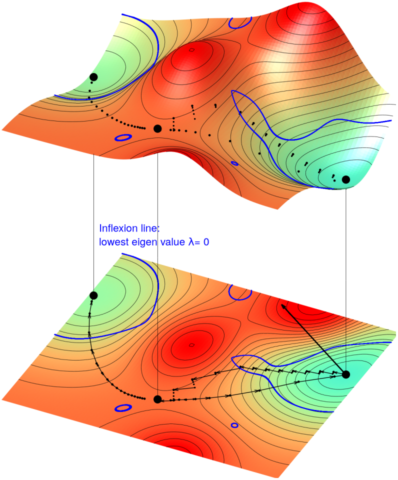


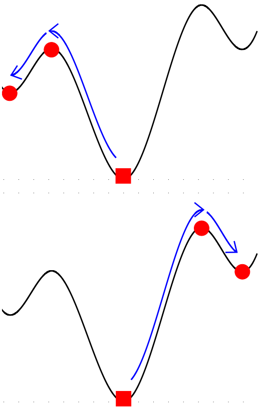




ARTn: Algorithm

ARTn: possibilities

Explore the PES



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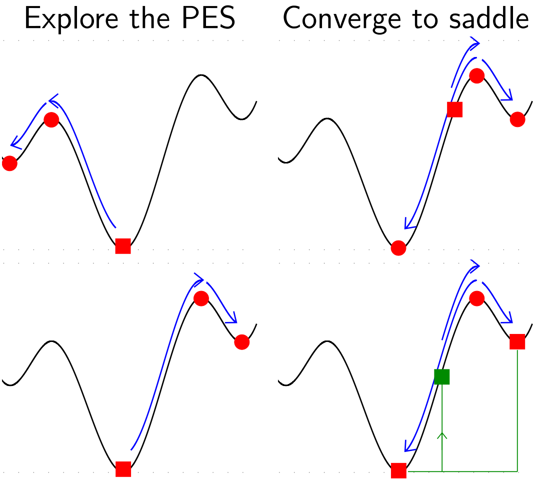

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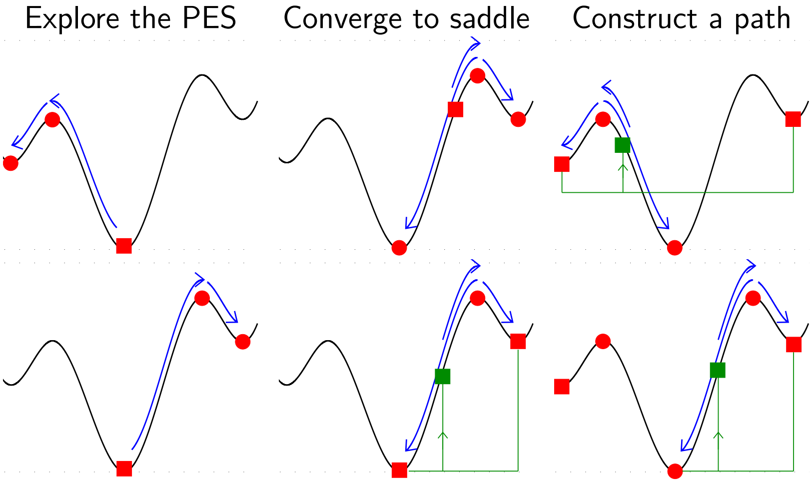
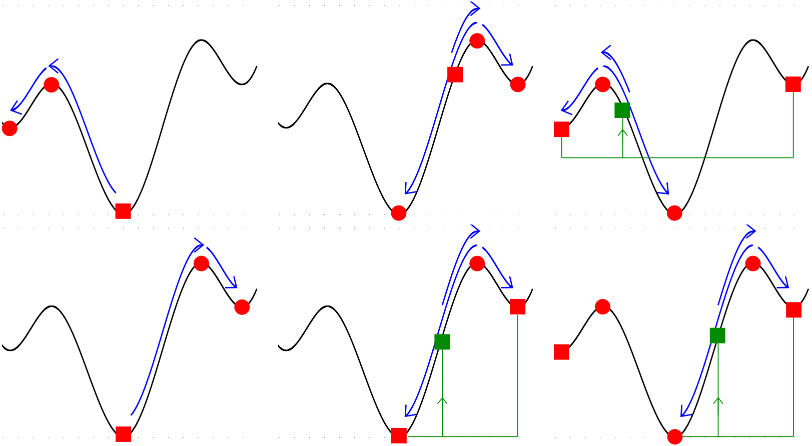


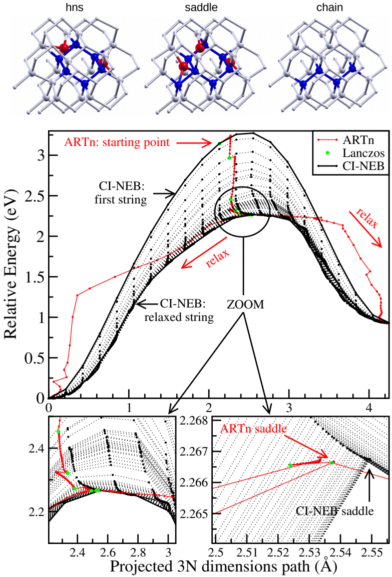
ARTn: possibilities

Explore the PES	Converge to saddle	Construct a path



not comparable	comparable	comparable

Comparison with NEB: Simple path



	force calc. (number)	Tot. force (Ry/au)
CI-NEB 5 im	1127	$1.1\ 10^{-3}$
CI-NEB 13 im	1976	$5.2\ 10^{-4}$
CI-NEB 19 im	2071	$1.9\ 10^{-4}$
ARTn	201	$1.1\ 10^{-5}$

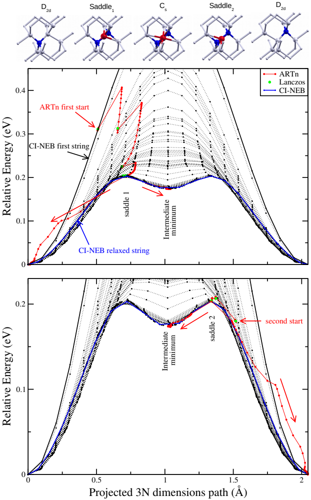
Can be 10 times faster

Can be 10 times more accurate

→ specially for winding paths

→ no arbitrary convergence

Comparison with NEB: Path with intermediate minimum



	force calc. (number)	Saddle 1 Tot. force (Ry/au)	Inter. min. Tot. force (Ry/au)	Saddle 2 (CI) Tot. force (Ry/au)
CI-NEB 5 im	273	$6.0\ 10^{-3}$	$2.4\ 10^{-3}$	$7.2\ 10^{-4}$
CI-NEB 13 im	1080	$6.0\ 10^{-4}$	$6.1\ 10^{-4}$	$4.7\ 10^{-4}$
CI-NEB 19 im	1539	$9.3\ 10^{-4}$	$2.1\ 10^{-3}$	$1.1\ 10^{-4}$
d-ARTn (total)	526	$3.0\ 10^{-6}$	$1.9\ 10^{-5}$	$1.0\ 10^{-5}$

ARTn is even better

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What is your favorite PES?

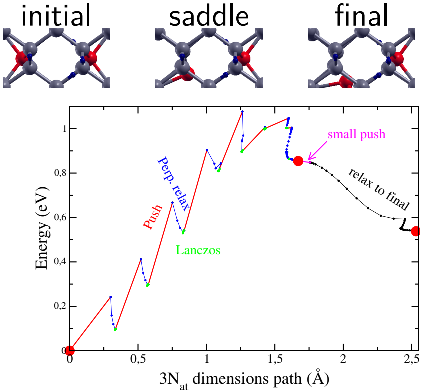
Smooth	Unsmooth

DFT
slow explo, accurate

Empirical potentials
fast explo, not accurate

Application

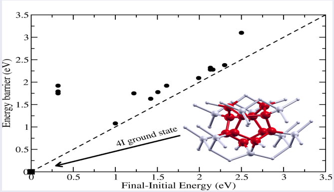
Metastable defect in silicon : 4V



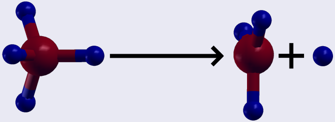
arrows = forces

Applications

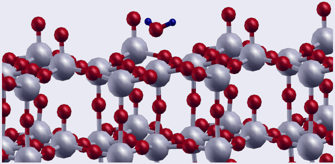
Metastable defects : 4I



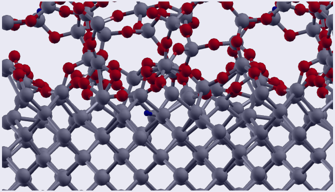
Molecules : $CH_4 \rightarrow CH_3 + H$



Surfaces : H_2O on WO_3



Interfaces : Si/SiO_2



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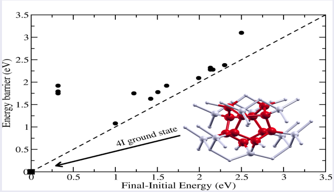

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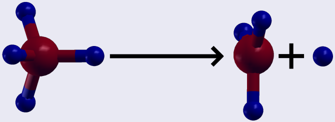

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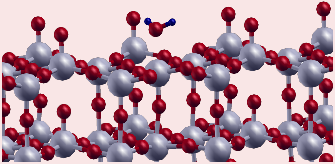

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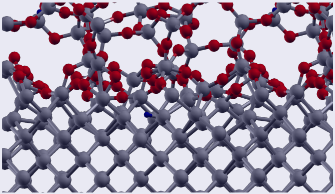
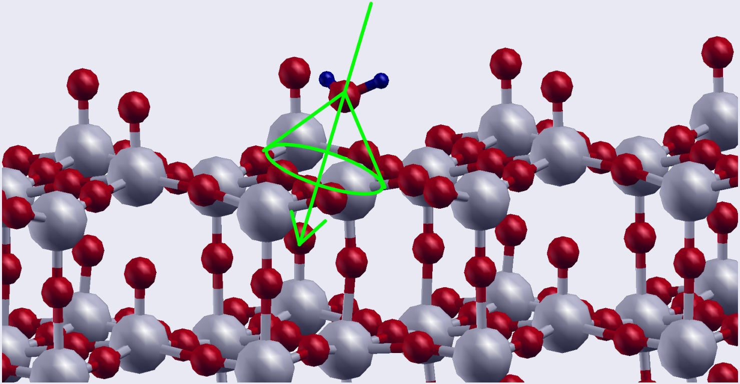


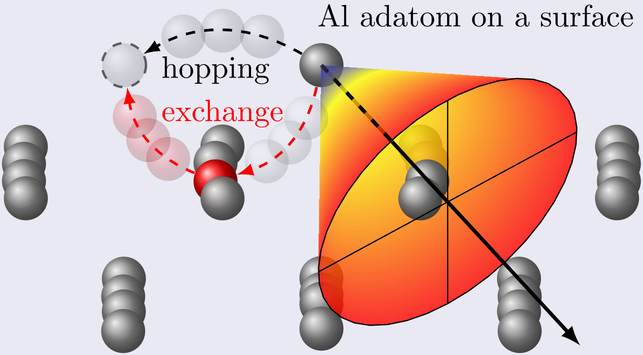
Restrict dimensions

Reaction on Surfaces: User guess



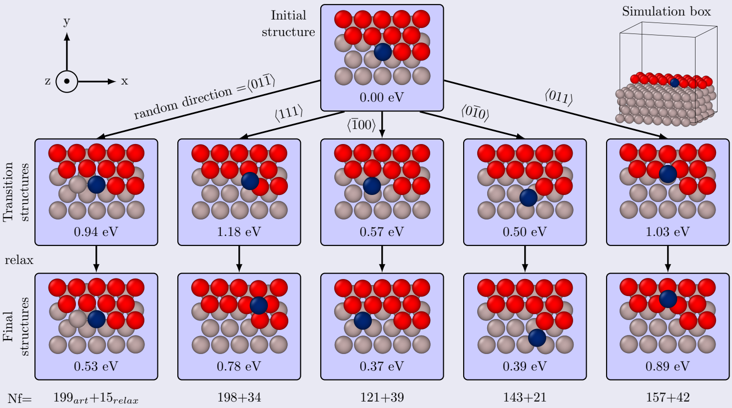
Restrict dimensions

Impose random conical direction

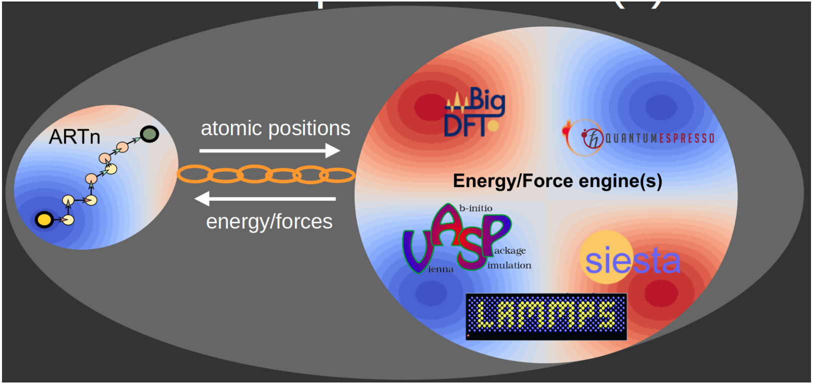


Restrict dimensions

Impose central atom(s)



Implementation



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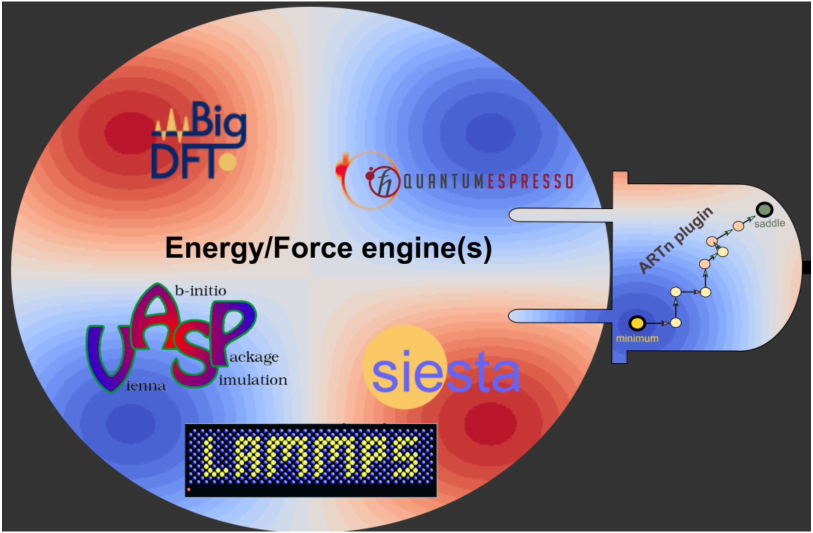


Free access to pART code and doc

https://gitlab.com/mammasmias/artn-plugin/

plugin-ARTn

Search docs

USER GUIDE

- Introduction
- Installation
- Input Parameters
  - List of ARTn input parameters
  - E/F engine inputs
- Output
- Troubleshooting
- Examples

PROGRAMMER GUIDE

- Plugin Philosophy
- pARTn Extension
- Code Organization
- List of plugin subroutines
- List of E/F interfaces
- List of parameters
- The pARTn API

Input Parameters / List of ARTn input parameters

List of ARTn input parameters

The ARTn parameters are given in the file *artn.in*. That file is formatted as FORTRAN NAMELIST, called *ARTN_PARAMETERS* as for example:

```
&ARTN_PARAMETERS
            ... specify parameters ...
/
```

All parameters available in pARTn are listed below, grouped by the part of ARTn algorithm they affect.

I/O control

- *verbose*
- *engine_units*
- *struc_format_out*
- *delr_thr*

Exploration Option

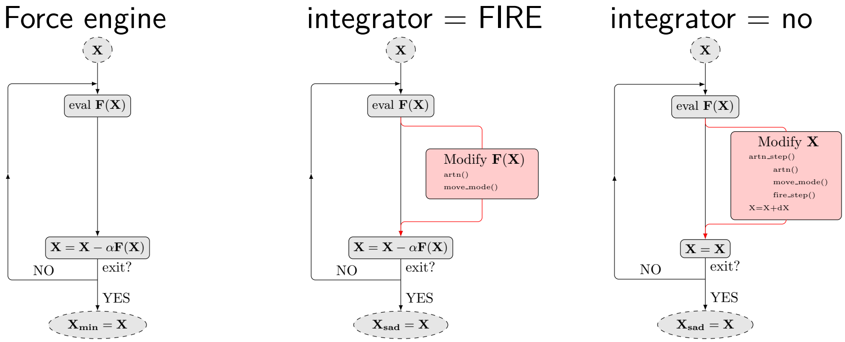
- *lrestart*
- *lpush_final*
- *lmove_nextmin*
- *zseed*
- *etot_diff_limit*

Control initial push

- *push_mode*
- *push_ids*
- *push_add_const*
- *push_dist_thr*
- *push_step_size*
- *push_step_size_per_atom*
- *push_guess*
- *ninit*

Control the Lanczos algorithm

Add plug to get SP: biased minimization



Minimal modification of the force engine:

- 1 call to routine
- 1 flag for the compilation
- 1 include location of the library

typical scripts

LAMMPS

```
units metal
dimension 3
boundary p p p
atom_style atomic
atom_modify sort 0 1

read_data Al_vac.data

pair_style eam/alloy
pair_coeff * * AlO.eam.alloy Al

plugin load ../../lib/libartn-lmp.so
fix 10 all artn alpha0 0.2 dmax 5.0

min_style fire
minimize 1e-4 1e-5 1000 10000
```

Execution:

```
mpirun -np 4 lmp_mpi -in lammps.in
```

Quantum Espresso

```
&CONTROL
calculation = 'relax',
/
&SYSTEM
celldm(1) = 7.6533908,...
/
&ELECTRONS
/
&IONS
ion_dynamics = 'fire',
/
ATOMIC_SPECIES
Al 1.0 Al.pz-vbc.UPF
ATOMIC_POSITIONS (angstrom)
Al 0.01 0.00 -0.07
...
K_POINTS gamma
```

Execution:

```
mpirun -np 4 pw.x -partn < relax.in
```

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  → Use ARTn
- You have no money (= CPU time)?
  → Use ARTn
- You want to explore the PES?
  → Use ARTn
- No arbitrary convergence
  → can reach any forces
- Use the DFT coupling, Quantum Espresso now
  → Plugin ∀ softwares in development (VASP, Abinit···)
- Empirical potentials: good for harmonic areas, bad for saddle points
  → Perfect for Machine Learning training

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PES badly defined:

- Not smooth empirical potentials
- Many small minima→ increase Lanczos *dr*
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Questions time

Canada

Italy

France

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Thank you for your attention

questions  suggestions