Kinetic Monte Carlo and Applications to Materials Development

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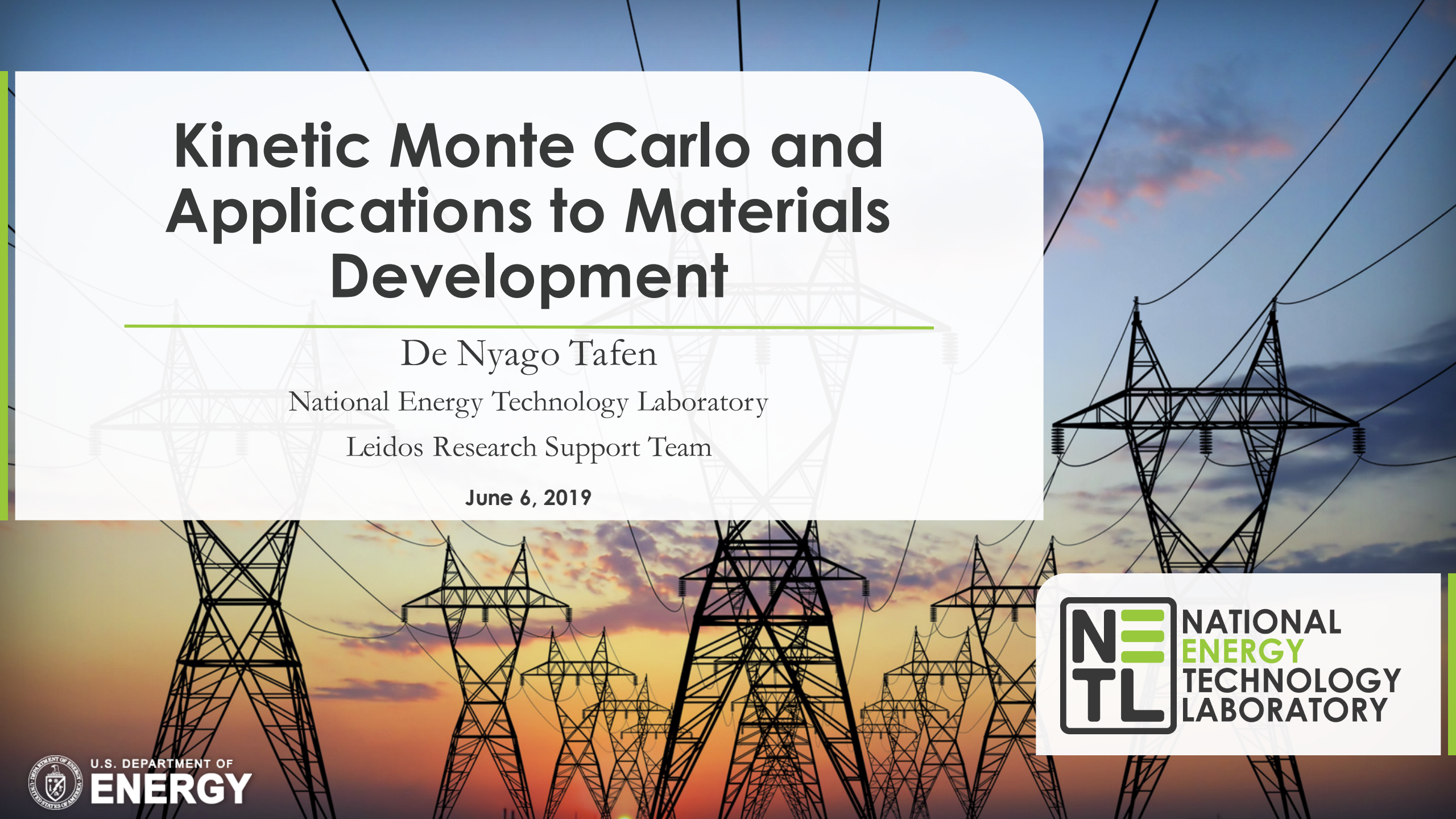

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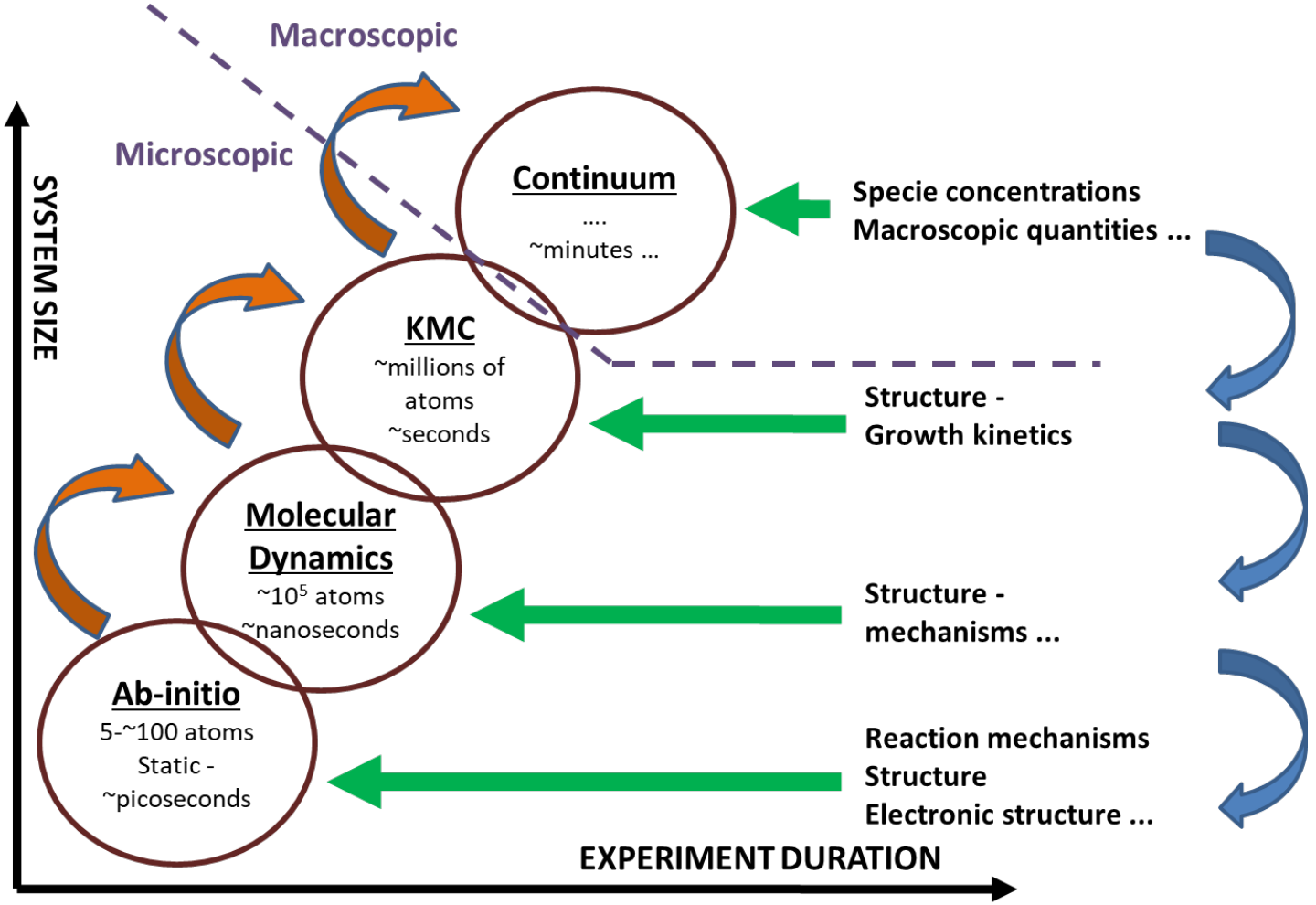
Outline

- Generals
- Kinetic Monte Carlo
- Applications

Generals

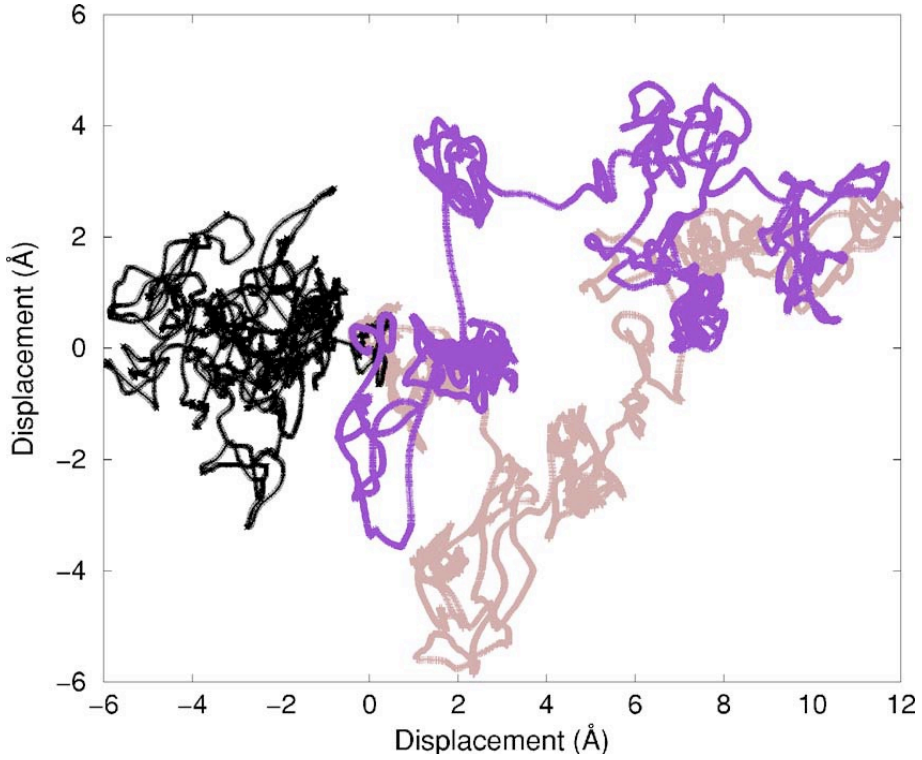
Tools for Materials Design



Generals

Molecular Dynamics -- MD

- **High-frequency motion dictates time-steps (e.g., vibrations).**
- **Time step is short: pico-seconds.**
- **Slow thermally-activated processes, such as diffusion, cannot be modeled.**



Trajectories of the most (indigo and brown) and least (black) mobile Ag atoms in $(GeSe_3)_{0.85}Ag_{0.15}$ glass (T=1000 K) after 62.5 ps.

Generals

Monte Carlo (MC) Methods

- What is Monte Carlo?
  - Simulation that uses random numbers to solve a given problem
  - stochastic (non-deterministic) dynamics.

- There is no time in Metropolis MC and the method cannot be used to study evolution of the system or kinetics.

- MC Time Step cannot be related to real time.

Generals

Equilibrium Monte Carlo

- Metropolis = random walks probing phase space
- Considering the transition from state

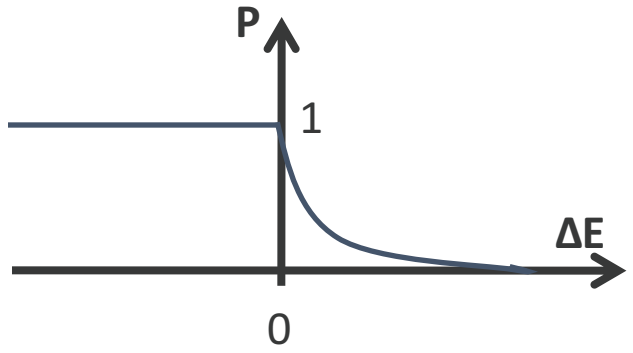
  $A = \{x_1, \dots, x_i, \dots, x_N\}$ to state $B = \{x_1, \dots, y_i, \dots, x_N\}$

  accompanied with a change $\Delta E = E_B - E_A$ in energy

- If $\Delta E \leq 0$, the transition is accepted
- If $\Delta E > 0$, a uniform random number $r \in]0,1]$ is chosen,

  if $r < \exp(-\Delta E/k_B T)$ the transition is accepted

  if $r > \exp(-\Delta E/k_B T)$ the transition is rejected



$$P(A \rightarrow B) = \min [1, \exp(-\Delta E/k_B T)]$$

Kinetic Monte Carlo

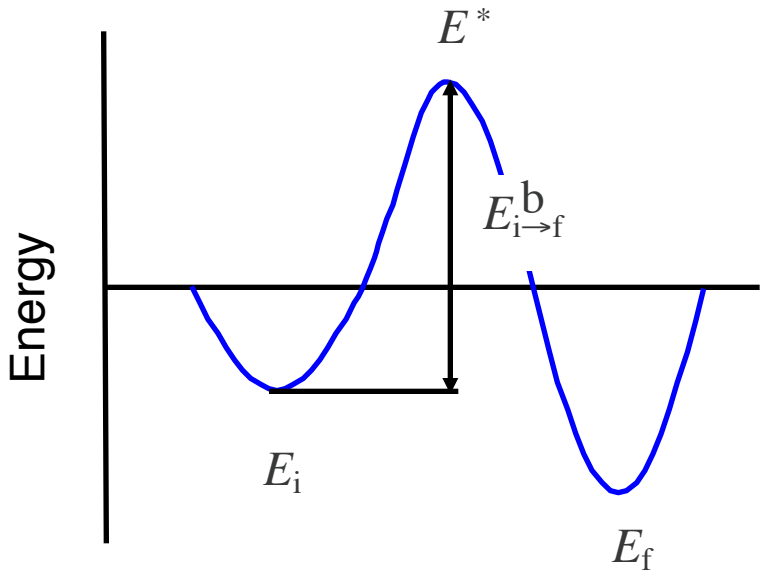
Fundamentals

- **The dynamics of Monte Carlo are taken seriously.**

- Time is introduced in the MC moves.
- Events with largest rate dominate, while low rate (low probability of occurrence) will be rare.

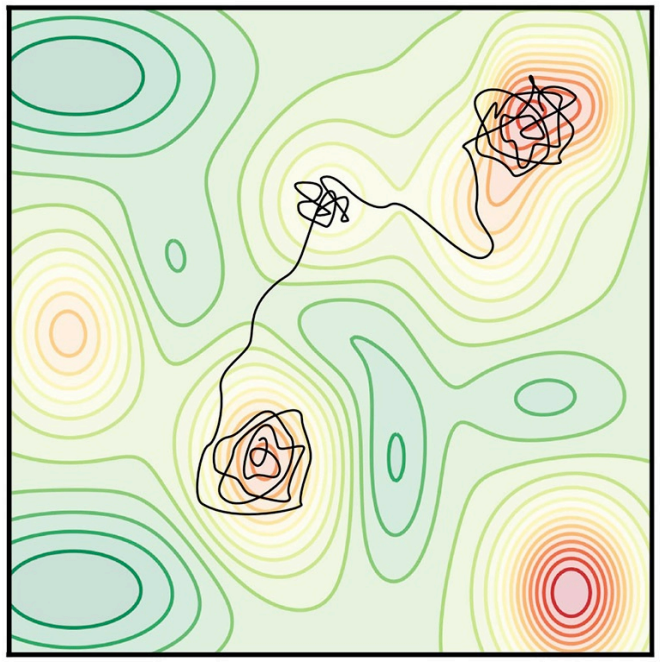
- We use transition rates that depend on the energy barrier between the states

- Detailed Balance must be met: Average rate of every microscopic process must exactly balance its reverse process.

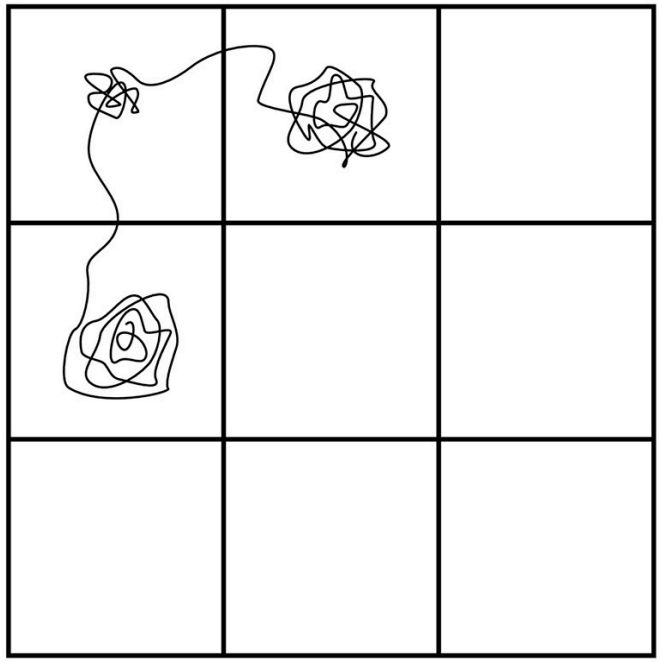


Kinetic Monte Carlo

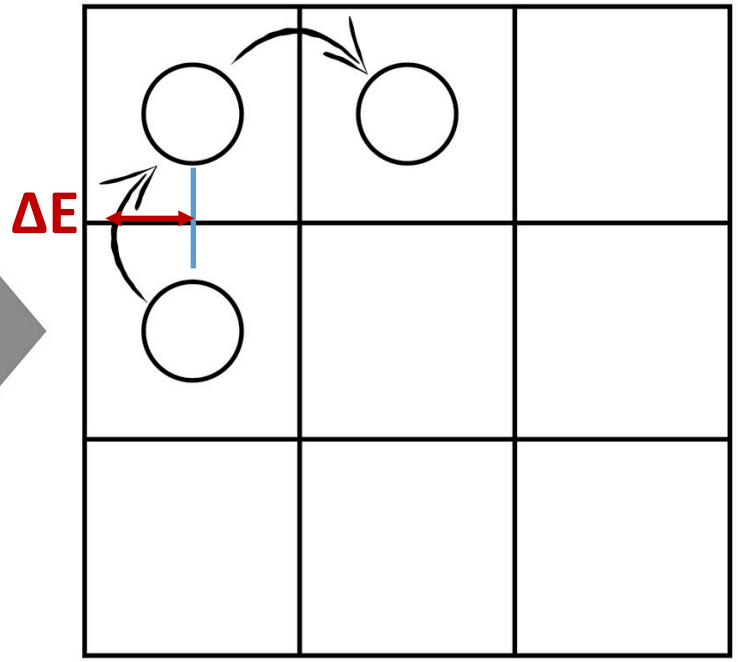
A Coarse-graining MD



MD trajectory overlaid on the underlying PES



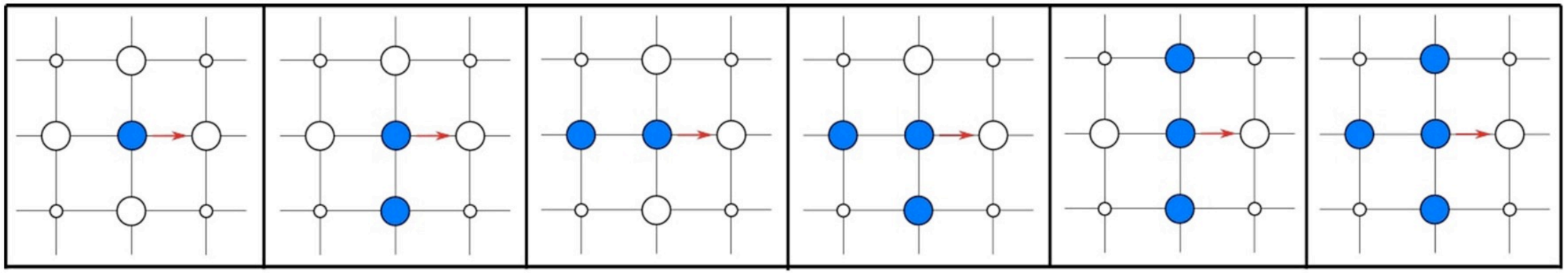
Coarse-graining of PES minima into positions on a defined lattice



Coarse-graining of the MD trajectory into a Markov chain of discrete hops between the basins/lattice positions. → kMC

Kinetic Monte Carlo

A Coarse-graining MD 2

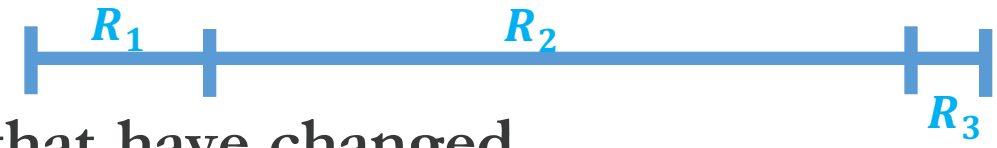


Hopping diffusion process of a particle on a quadratic lattice for all possible configurations of the nearest neighbor lattice sites in the initial state. Configurations that are equivalent by symmetry are shown only once. The site where the particle diffuses to must be empty for the process to be possible.

Kinetic Monte Carlo

Basic Bortz-Kalos-Liebowitz (BKL) algorithm -- **Sampling of the Event**

1. Time t = 0
2. Establish a list of all possible transition states and calculate the cumulative function $R_i = \sum_{j=1}^{i} k_i$ for i=1,…,N total number of transitions
3. Get a uniform random number u
4. Find the event by finding out the i such that $R_{i-1} < uR \leq R_i$
5. Occurrence of the event i



6. Find all transitions and associated rates that have changed
7. Get a uniform random number z =]0,1]
8. Update the time with t = t + Δt where Δt = - log z / R
9. Return to step 2

Bortz et al. J. Comp. Phys. 17, 10 (1975)

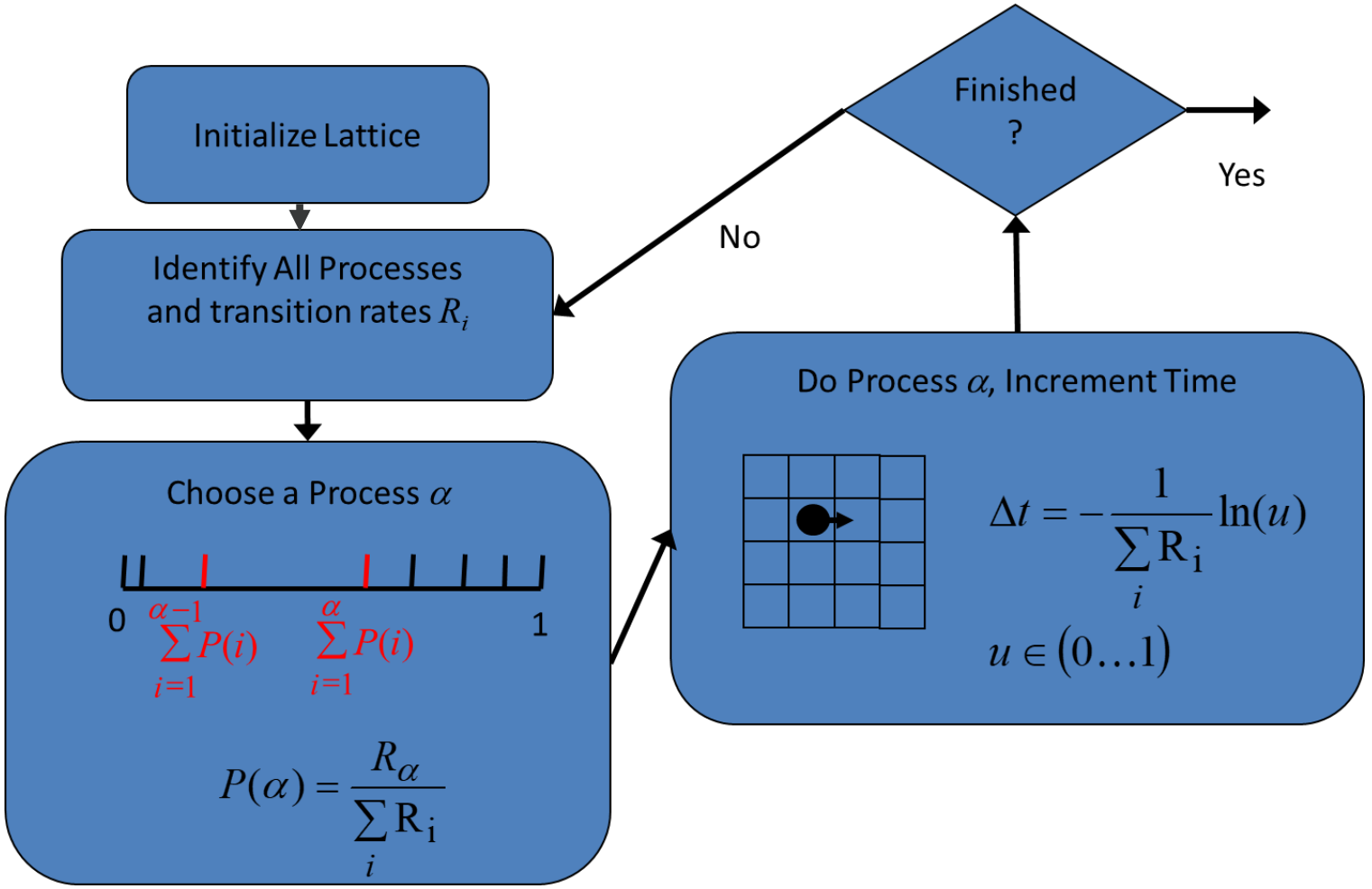
Kinetic Monte Carlo

Alternative Algorithm -- **Sampling of Time**

1. Time t=0
2. Form a list of all possible transition states and calculate all possible rates
3. Schedule these transitions for all system sites
4. Choose the time minimum
5. Carry out the associated (site, event i)
6. Update the time with $t = t + \Delta t$ where $\Delta t = -\log(z) / k_i$
7. Change the rate of all sites that have been modified due to event i
8. Update the scheduler
9. Return to step 2

Kinetic Monte Carlo

Flowchart for BKL



*Binary Tree Search
*N-Fold Way

Bortz et al. J. Comp. Phys. 17, 10 (1975)

KMC Fields of Applications

Examples

- Magnetism (the original application)
- Surface and bulk diffusion
- Molecular Beam Epitaxy growth (MBE)
- Chemical Vapor Deposition (CVD)
- Defects formation and diffusion
- Oxidation (thermal growth, Atomic Layer Deposition techniques)
- …

KMC Applications

Simple Adsorption & Desorption of Atoms on Surface

- We assume:
  - Adsorbed molecules do not interact
  - Molecule arrives at surface at random, uncorrelated times characterized by average rate r_A, similarly for desorption.
  - The surface coverage (or probability of adsorption) is given by:

$$\frac{d\theta(t)}{dt} = r_A[1-\theta(t)] - r_D\theta(t)$$

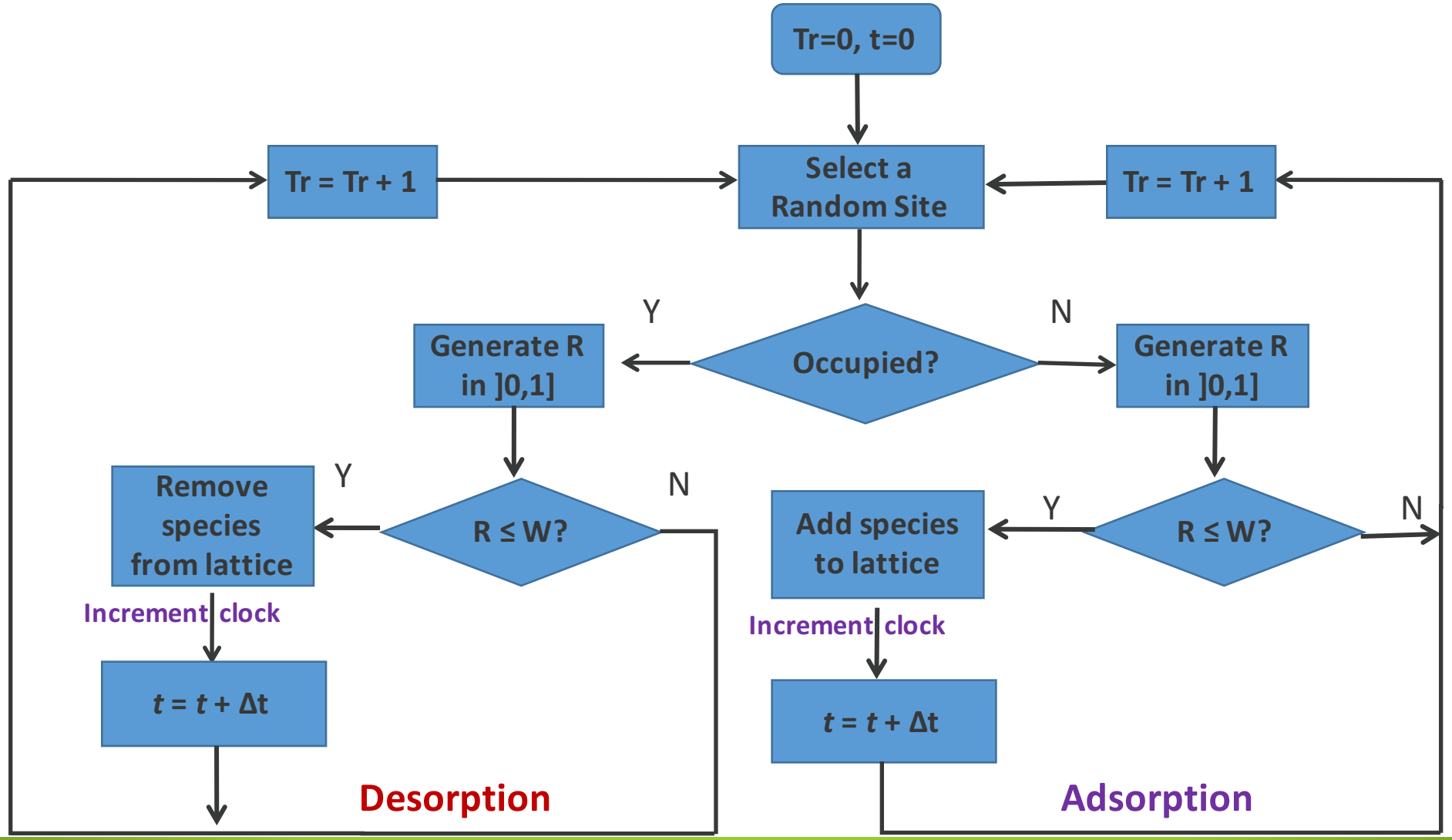
  - Analytic solution $\theta(t) = \frac{r_A}{r_A + r_D}\left[1 - e^{-(r_A+r_D)t}\right] \xrightarrow[t\to\infty]{} \frac{r_A}{r_A + r_D}$

  - Transition Probabilities W_A and W_D should obey detailed balance since they are chosen at random and independently such that successful adsorption is $W_A[1-\theta(t)]$ and desorption is $W_D\theta(t)$.

  - Average adsorption in T trials is $\langle N_{A,T}\rangle = W_A[1-\theta(t)]T$
  - At steady-state $\langle N_{A,T}\rangle = \langle N_{D,T}\rangle$ or $W_A[1-\theta] = W_D\theta$. Detailed Balance!

Adsorption & Desorption of Atom on Surface

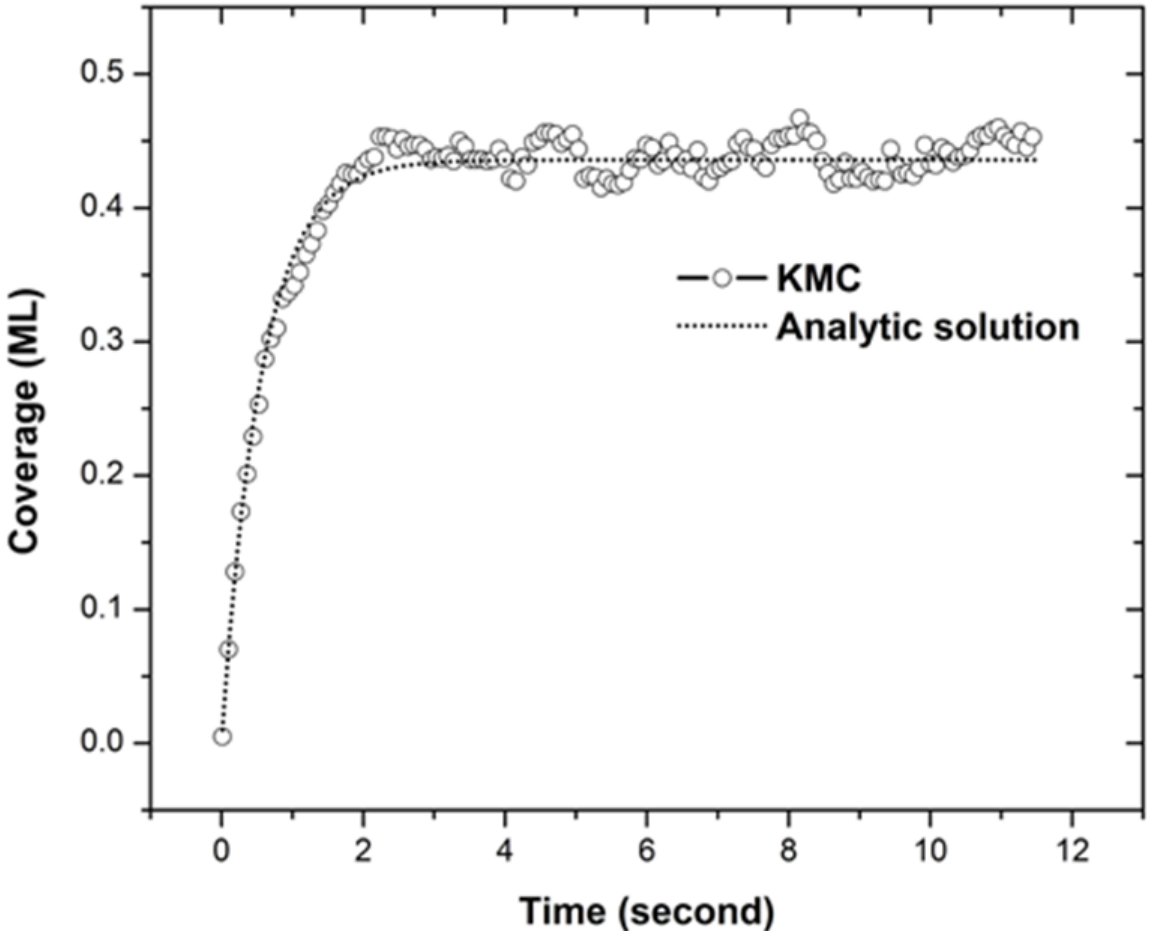
Flowchart



Adsorption & Desorption of Atom on Surface

Adsorption & Desorption Processes

- Circles: Solutions obtained by the kMC algorithm
- Dots: Solutions obtained by solving directly differential equation
- Adsorption rate: $r_A = 0.775129$ (event/site/s)
- Desorption rate $r_D = 1.00301$ (event/site/s).

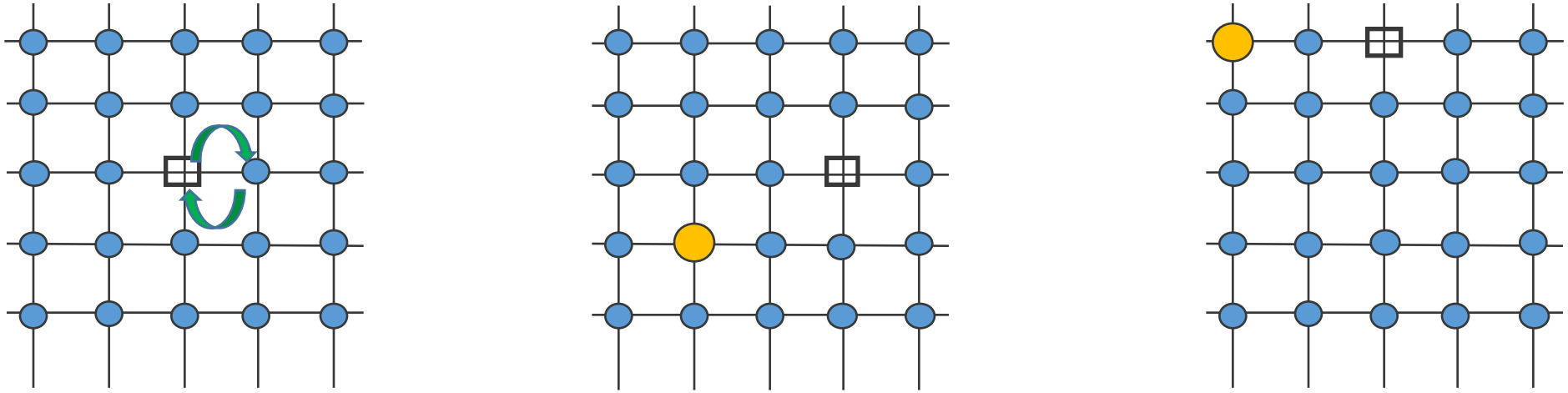


Hong et al. J. Catal. 276, 371 (2010)

kMC - Vacancy Mediated Diffusion

Definition of the problem

- Diffusion in solids is a complex thermally activated process which can occur through a variety of mechanisms.
- Let's apply kMC to a vacancy mediated diffusion in which a vacancy undergoes a random walk through a discrete atomic square lattice.
- In this case the vacancy moves by swapping positions with neighboring atoms.

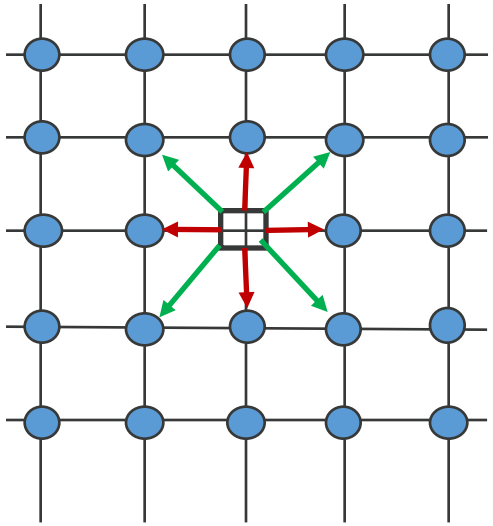


- We choose at random an atom to trace and keep its position through the kMC simulation; we can estimate quantities like diffusion coefficients.

kMC - Vacancy Mediated Diffusion

kMC Steps

1- Identify all relevant processes for your system



8 clearly defined processes:

- Red arrows: P_{X1}, P_{X2}, P_{X3}, P_{X4}, with energy barrier E_X
- Green arrows: P_{Z1}, P_{Z2}, P_{Z3}, P_{Z4}, with energy barrier E_Z

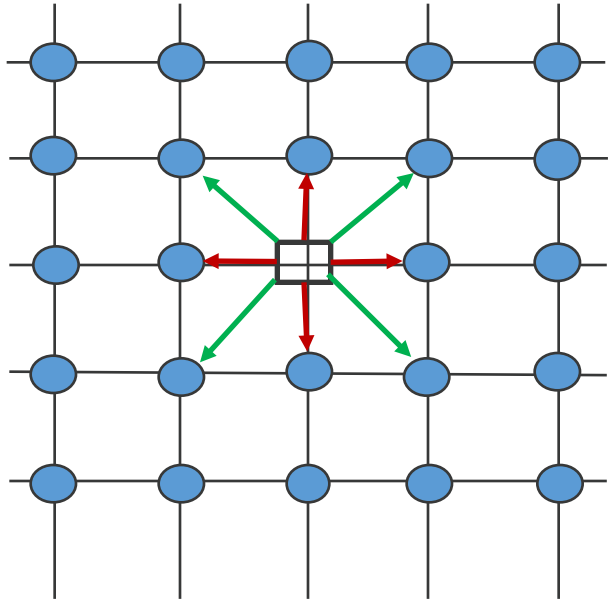
Other possible processes:

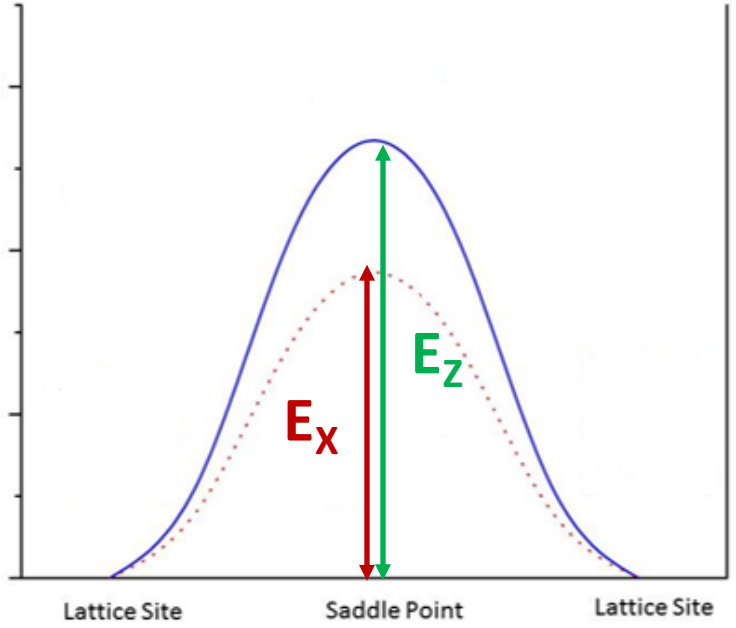
- Atoms swap position with each other
- Vacancy destruction (adsorption) or creation (desorption)
- etc

kMC - Vacancy Mediated Diffusion

kMC Steps – Energy barriers

2- Determine the energy barrier for each process. We can use transition state theory (TST) to calculate a rate for each process, k_i for the process i.





kMC - Vacancy Mediated Diffusion

kMC Steps – Rate and Time

3- Calculate the total rate of all the processes.

$$R = \sum_i k_i = 4\nu_X exp(-\beta E_X) + 4\nu_Z exp(-\beta E_Z)$$

$$\beta = {}^{1}/_{k_B T}$$

4- Choose from a Poisson distribution using R the time at which the next event happens.

- Draw a random number u ϵ]0,1]
- $t = -\frac{1}{R} \ln u$

kMC - Vacancy Mediated Diffusion

kMC Steps -- Event

5- Choose from the rate catalog event that actually happens. This is done by generating a second random number.

$$p_{X1} = \frac{k_{X1}}{R} = \frac{\nu_X exp(-\beta E_X)}{4\nu_X exp(-\beta E_X)+4\nu_Z exp(-\beta E_Z)}$$

$$p_{X2} = \frac{k_{X2}}{R} = \frac{\nu_X exp(-\beta E_X)}{4\nu_X exp(-\beta E_X)+4\nu_Z exp(-\beta E_Z)}$$

$$p_{X3} = \frac{k_{X3}}{R} = \frac{\nu_X exp(-\beta E_X)}{4\nu_X exp(-\beta E_X)+4\nu_Z exp(-\beta E_Z)}$$

$$p_{X4} = \frac{k_{X4}}{R} = \frac{\nu_X exp(-\beta E_X)}{4\nu_X exp(-\beta E_X)+4\nu_Z exp(-\beta E_Z)}$$

$$p_{Z1} = \frac{k_{Z1}}{R} = \frac{\nu_Z exp(-\beta E_Z)}{4\nu_X exp(-\beta E_X)+4\nu_Z exp(-\beta E_Z)}$$

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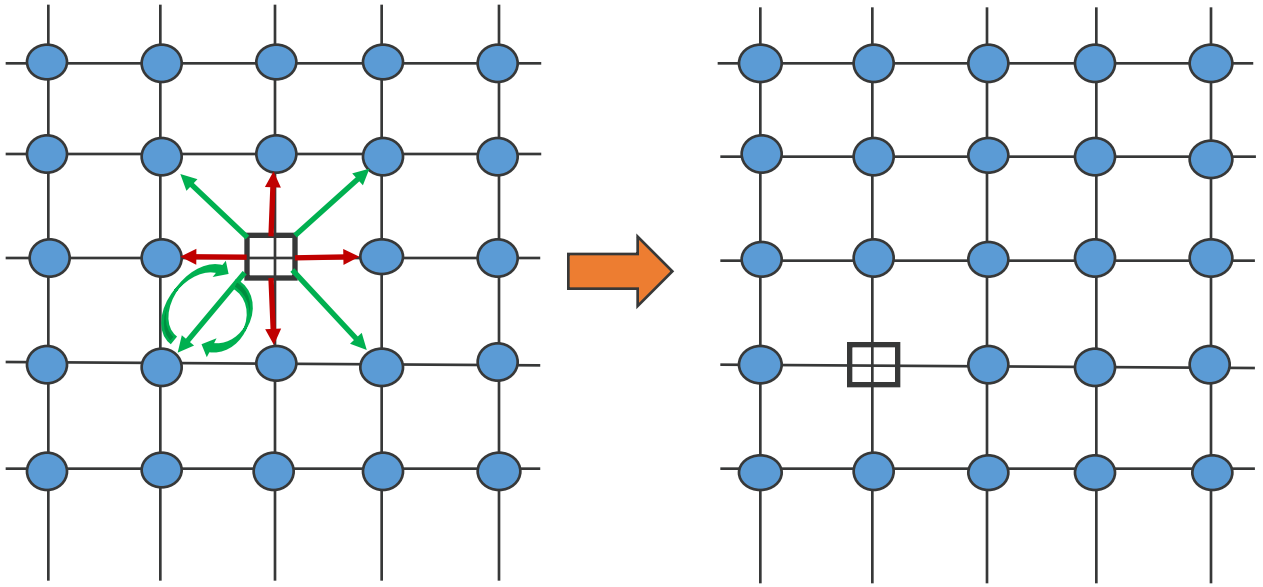


Advance the clock, update the configuration and record data for your properties of interest.

kMC - Vacancy Mediated Diffusion

kMC Steps

6- Repeat the process as long as it's necessary to obtain reasonable results.

Atomic Diffusion in fcc NiAl Binary Alloys

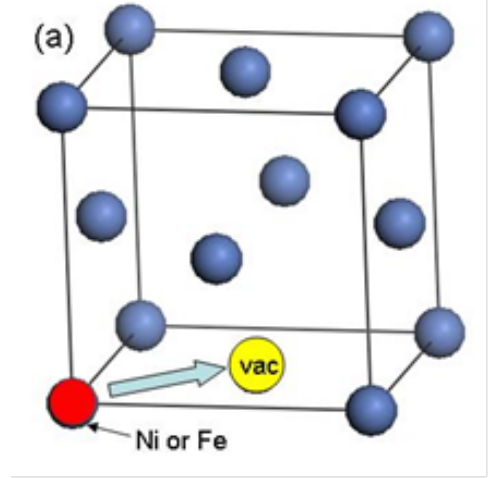
Energy barriers and Rates

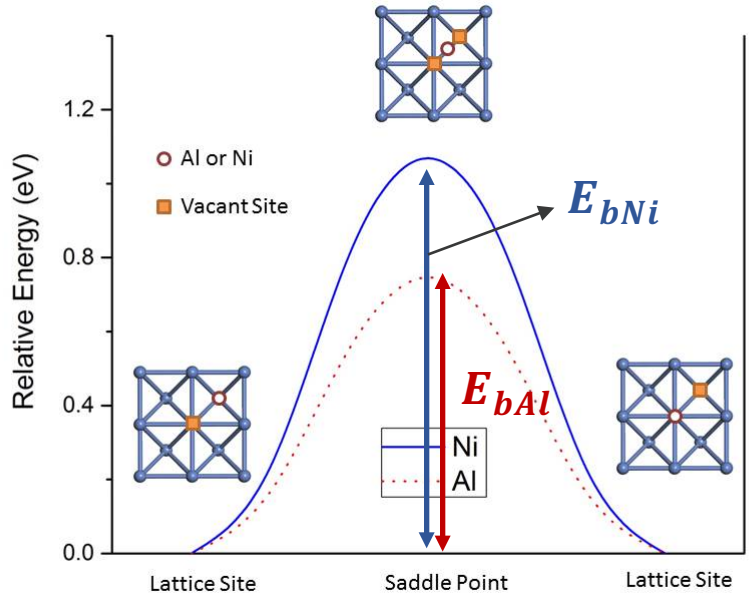
- Hopping rates

$$k_i = \nu_0 exp\left(-\frac{E_{bi}}{k_B T}\right)$$

$$\nu_0 = \frac{k_B T}{h}\frac{q^{+}_{vib}}{q^{0}_{vib}}$$

- ν_0 and E_b are obtained from DFT
- TST satisfies Detailed Balance and Kinetics

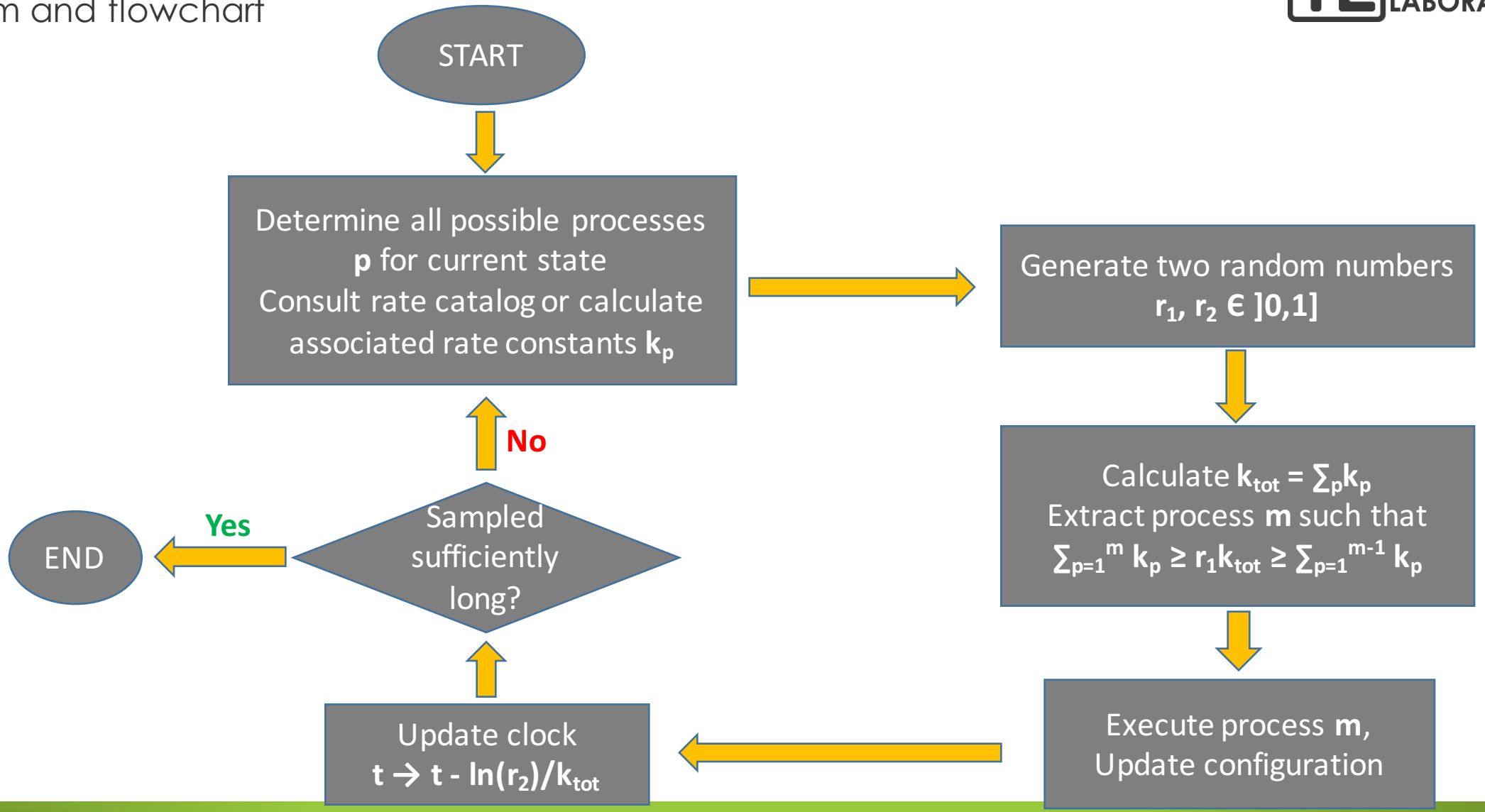




Alfonso & Tafen, J. Phys. Chem. C 119, 11809 (2015)

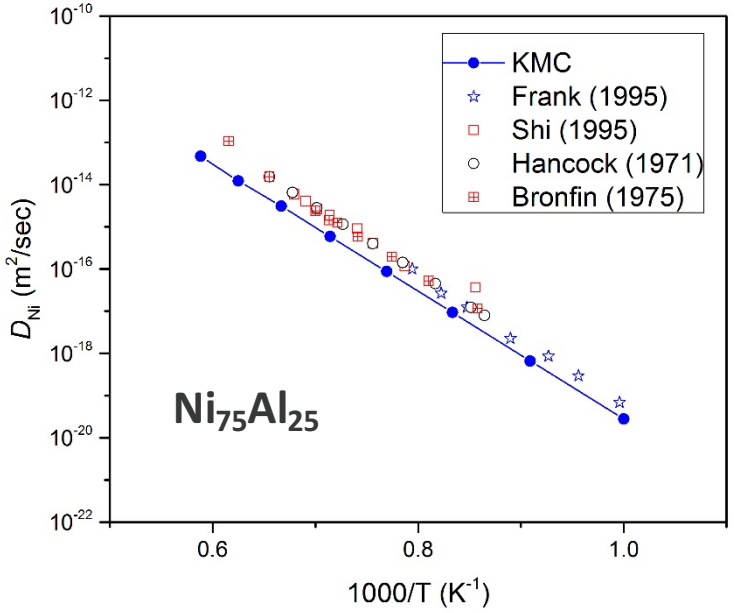
Atomic Diffusion in fcc NiAl Binary Alloys

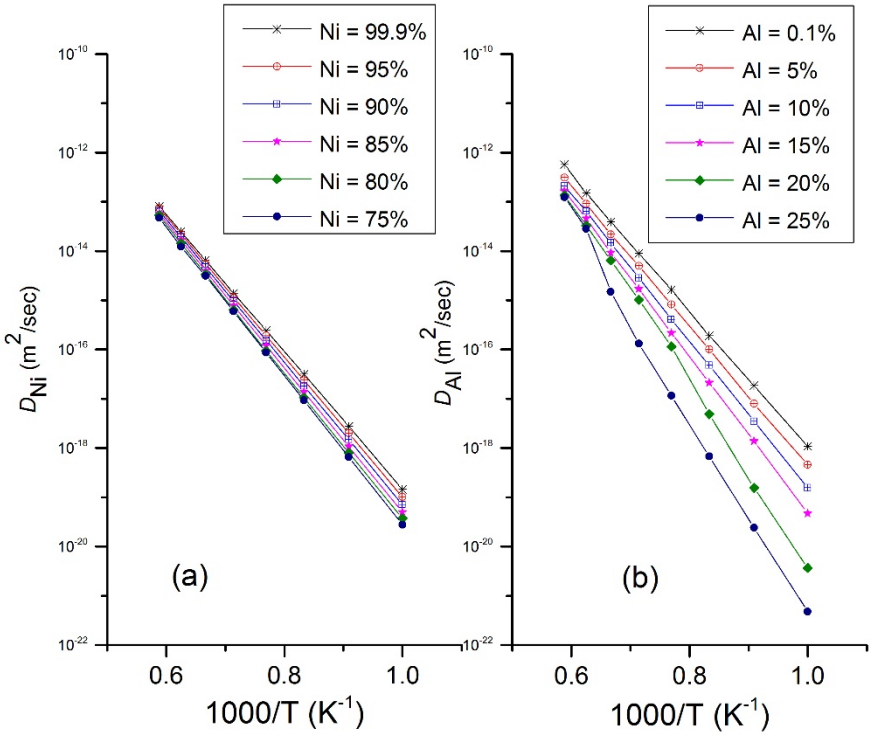
Algorithm and flowchart

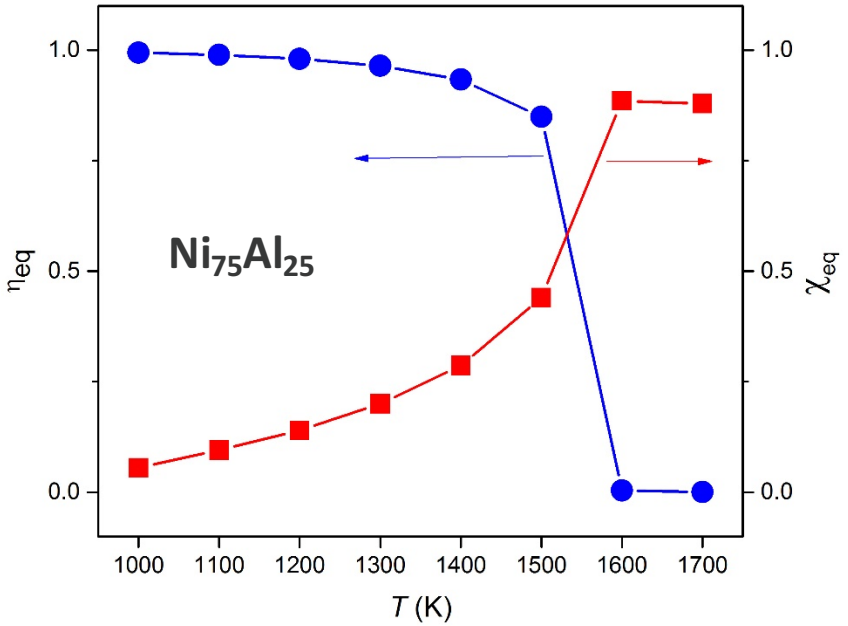


kMC Applications

Ni & Al diffusion in NiAl alloy







Diffusion Coefficient

$$D = \lim_{t\to\infty} \frac{1}{6t} \left\langle \sum_{t=0}^{\infty} [\vec{r}(t+\Delta t) - \vec{r}(t)]^2 \right\rangle$$

Long range order

$$\eta = 1 - \frac{N_{Ni}^{(Al)}}{0.75 \times N^{(Al)}}$$

Short range order

$$\chi = \frac{N_{NiAl}^{(Al)(Ni)}}{N_{Ni}^{Al}}$$

Alfonso & Tafen, J. Phys. Chem. C 119, 11809 (2015)

Conclusions

Advantages and limitations

- kMC is a coarse-grained technique for condensed-matter dynamics
- kMC simulates a Poisson Process
- kMC can be coupled with ab initio rate processes
- Relation to the experimental procedure
- Time follows mechanism changes…flexibility
- No requirement of thermodynamic equilibrium in the algorithm

There are pit-falls

- Mechanisms and associated activation barriers have to be known in advance
- Much effort in an efficient coding of the mechanisms, data structures, etc. … Forget transferability

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Questions?

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