Kinetic Monte Carlo Simulations of Surface Reactions

Thomas Young Centre Materials Modelling Course

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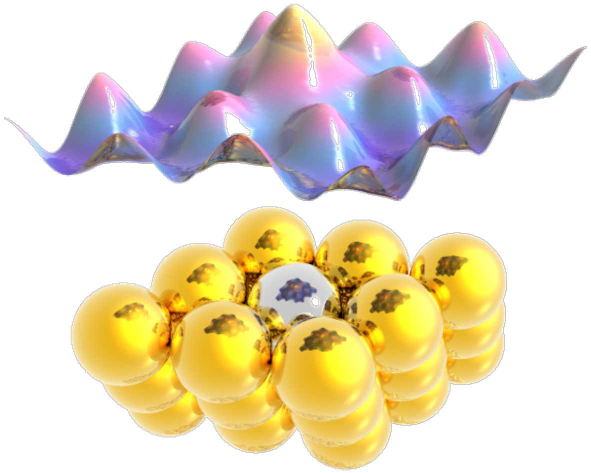
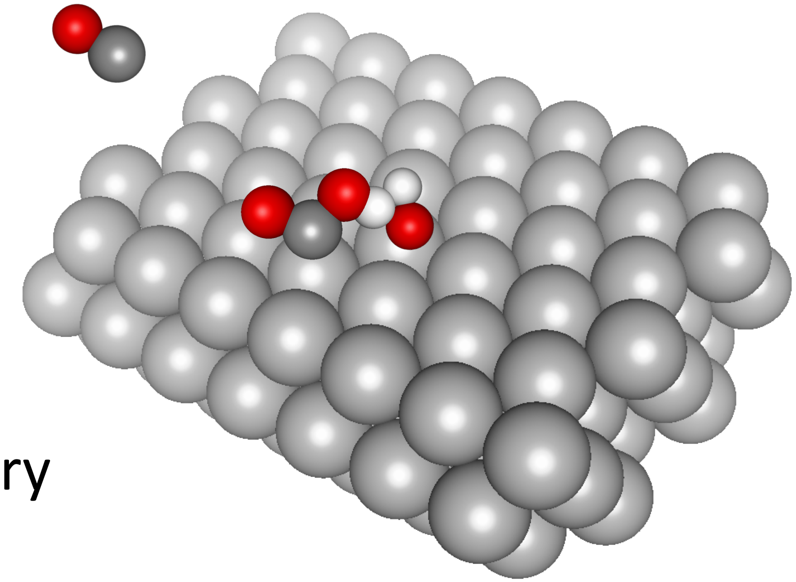
Why Do Kinetic Modelling in Catalysis and Surface Science?

- **DFT Calculations in Catalysis:**
  - ✓ Electronic structure of materials
  - ✓ Stability of intermediates
  - ✓ Chemical pathways and energy barriers

*Need "predictive models able to capture trends in **activity** and **selectivity**"*

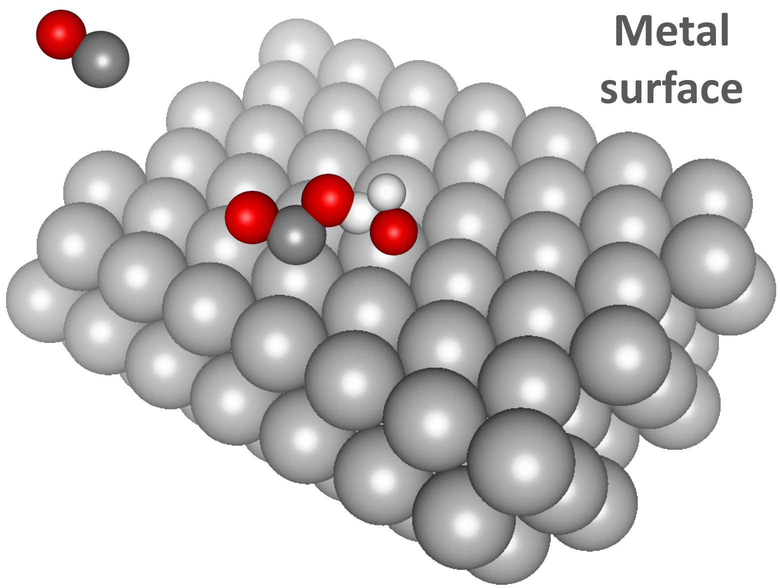




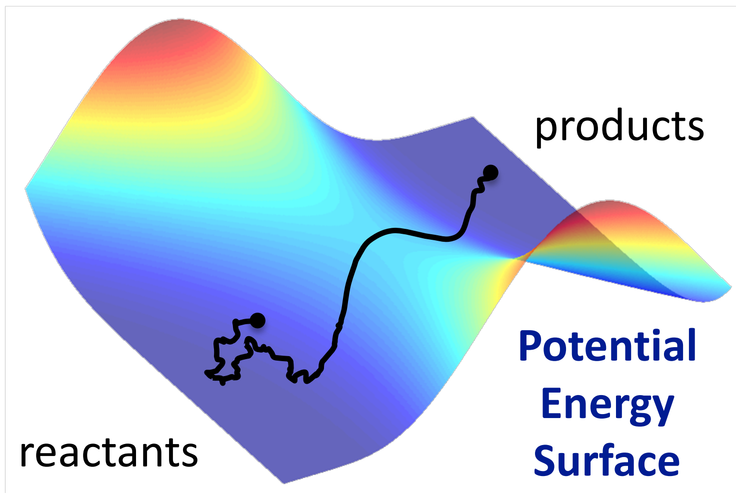
- Parallel or competing pathways?
- Temperature and pressure effects?
- Coverage effects on reaction rates?

→ **Kinetic modelling** necessary

The Kinetic Monte Carlo Approach



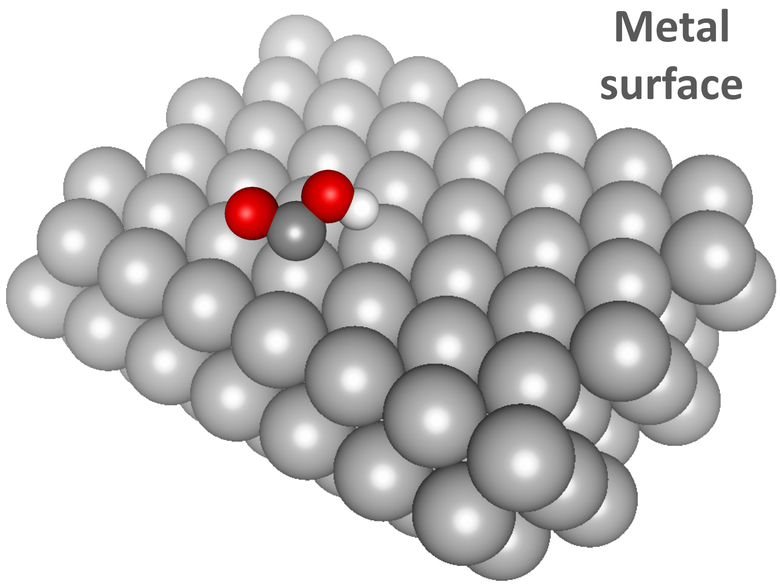
$CO_{(gas)} + OH^* \rightleftarrows COOH^*$



- Instead of simulating dynamics, KMC[1] focuses on rare events
- Simulates reactions much faster than Molecular Dynamics
- Incorporates spatial information contrary to micro-kinetic models[2]

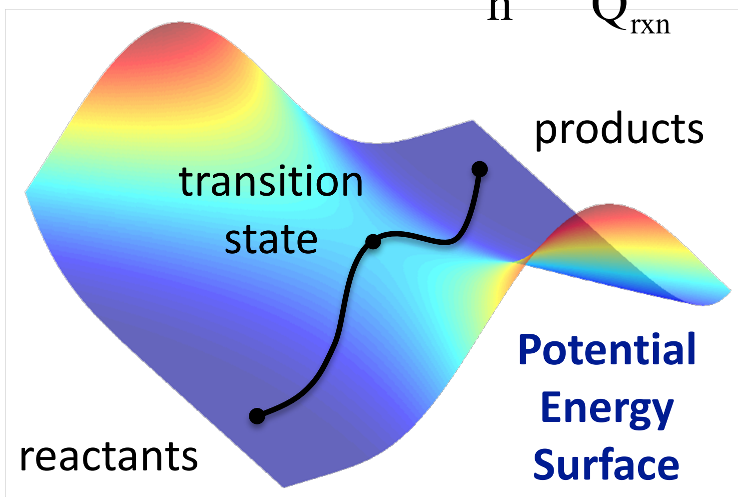
[1] M. Neurock and E. W. Hansen, Comput. Chem. Eng. 22, S1045 (1998); K. Reuter and M. Scheffler, Phys. Rev. Lett. 90: 046103 (2003); M. Stamatakis, J. Phys. Condens. Matter. 27: 013001 (2015).
[2] J. A. Dumesic et al., The Microkinetics of Heterogeneous Catalysis. (American Chemical Society, 1993).

The Kinetic Monte Carlo Approach



$CO_{(gas)} + OH^* \rightleftarrows COOH^*$

$$k_{rxn} = \kappa \cdot \frac{k_B \cdot T}{h} \cdot \frac{Q^\ddagger}{Q_{rxn}} \cdot e^{-\frac{\Delta E^\ddagger}{k_B \cdot T}}$$



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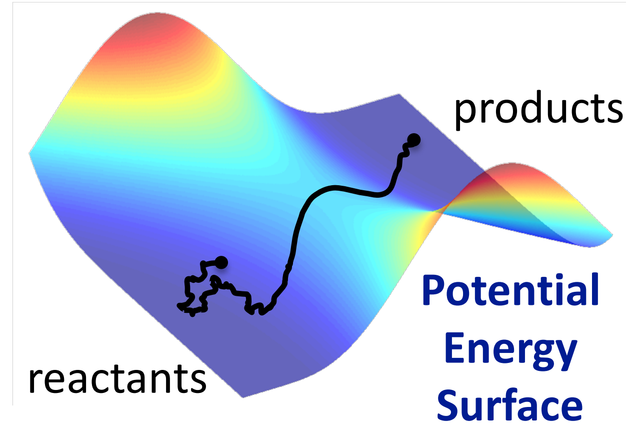
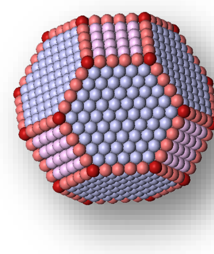
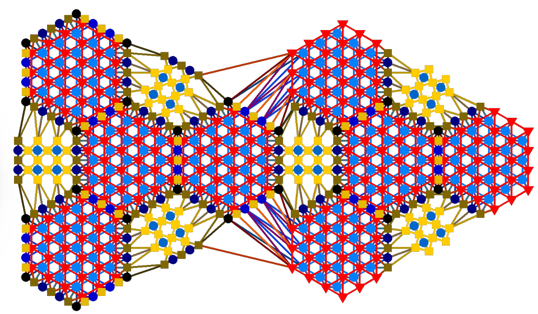
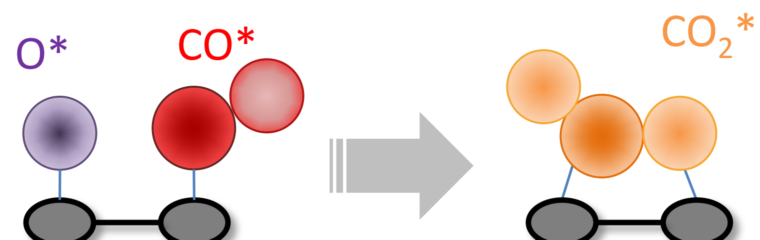
Outline

- Atomistic/Molecular level
  - Calculating rates for elementary events (transition state theory)
- Mesoscopic level
  - Simulating reactions on spatially extended systems
- Accurate modelling of catalytic surface reactions
  - Complex materials (lattices)
  - Complicated reactions
  - Coverage effects









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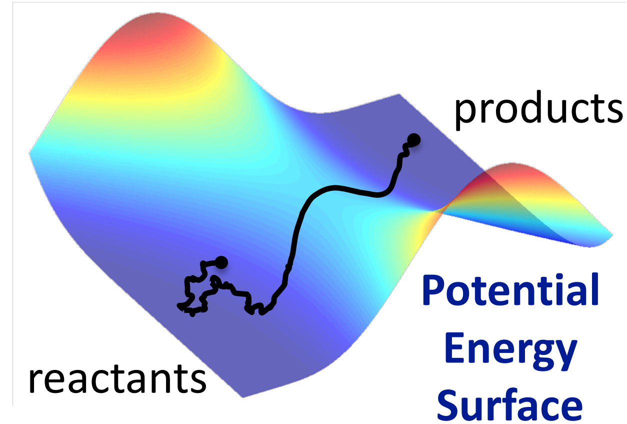
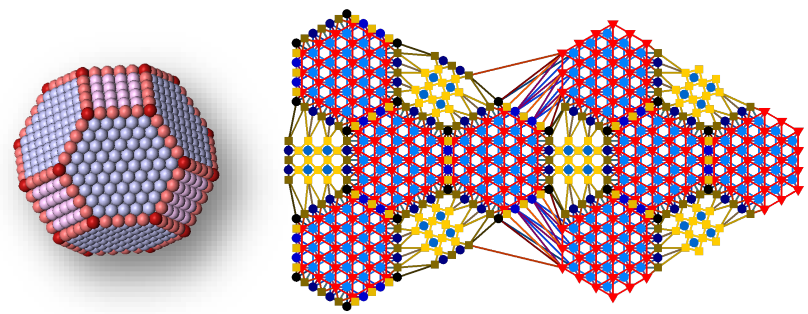
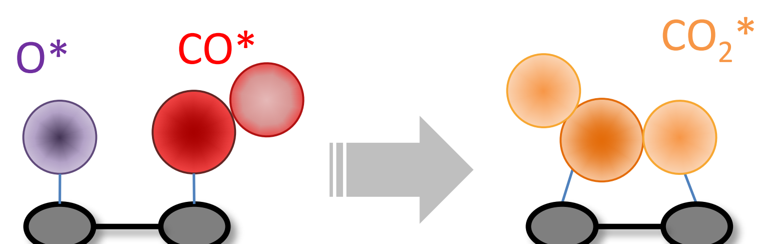


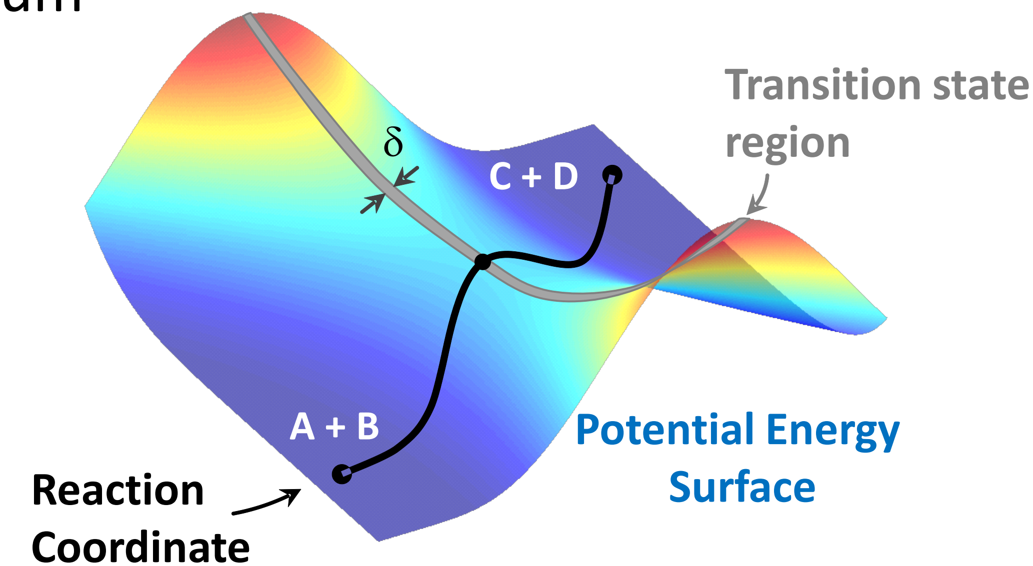




Transition State Theory

- **Assumption**: quasi-equilibrium between initial state and transition state:

$$A + B \rightleftarrows * \rightleftarrows C + D$$



$$\boxed{\frac{[*]}{[A]\cdot[B]} = \frac{Q_*}{Q_A \cdot Q_B}}$$

$$Q_A = \frac{1}{h^{3\cdot N_A}} \cdot \int \exp\left(-\frac{\mathcal{H}_A}{k_B \cdot T}\right) d\Gamma_A \quad \text{and} \quad Q_B = \frac{1}{h^{3\cdot N_B}} \cdot \int \exp\left(-\frac{\mathcal{H}_B}{k_B \cdot T}\right) d\Gamma_B$$

$$Q_* = \frac{1}{h^{3\cdot N}} \cdot \int \exp\left(-\frac{\mathcal{H}_*}{k_B \cdot T}\right) d\Gamma_* \quad \text{where} \quad N = N_A + N_B$$

P. Pechukas, Statistical Approximations in Collision Theory, *In* Dynamics of Molecular Collisions - Part B, W. Miller, ed. Springer 1976

Transition State Theory

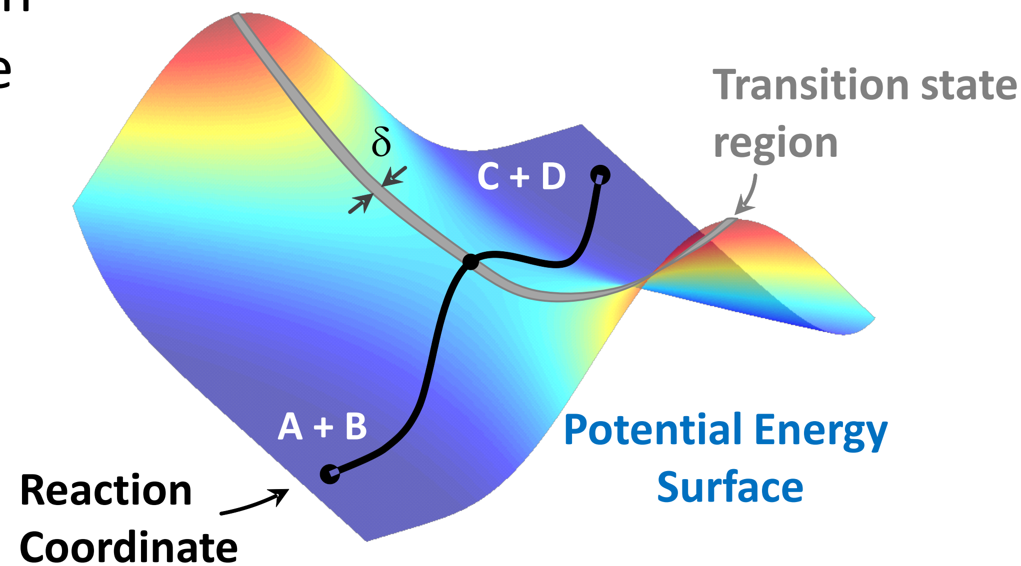
$$A + B \rightleftarrows * \rightleftarrows C + D$$

- **Assumption**: at the transition state the Hamiltonian can be expressed as:

$$\mathcal{H}_* = \frac{p^2}{2 \cdot m^*} + \mathcal{H}^\ddagger$$

kinetic energy (along reaction coordinate)

"everything else"



Therefore:

$$Q_* = \frac{\delta}{h} \cdot \frac{1}{h^{3 \cdot N - 1}} \cdot \int \exp\left(-\frac{\mathcal{H}^\ddagger}{k_B \cdot T}\right) d\Gamma^\ddagger \cdot \int_{-\infty}^{\infty} \exp\left(-\frac{p^2}{2 \cdot m^* \cdot k_B \cdot T}\right) dp$$

$$\boxed{Q_* = \frac{\delta}{h} \cdot Q^\ddagger \cdot \sqrt{2 \cdot \pi \cdot m^* \cdot k_B \cdot T}}$$

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Transition State Theory

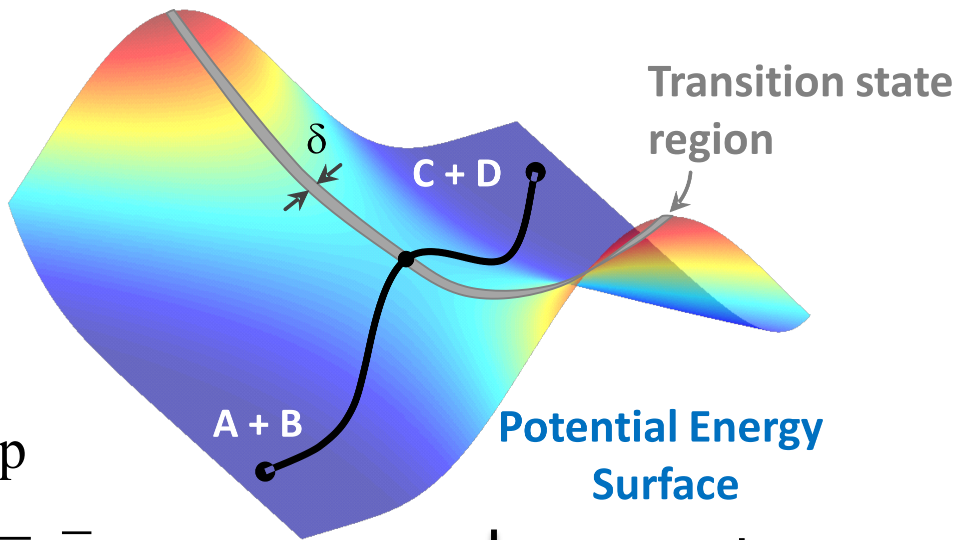
- Now number of transitions from reactants to products per unit time is (on average):

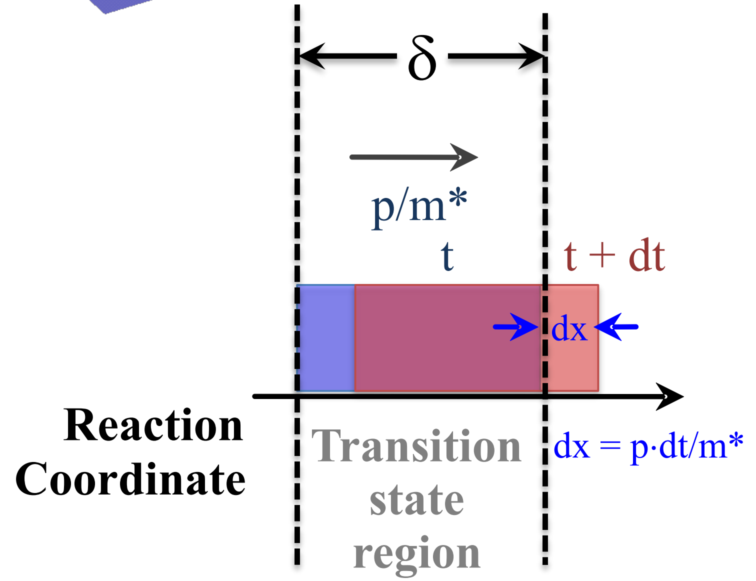
$$\mathrm{A+B} \rightleftarrows * \rightleftarrows \mathrm{C+D}$$

$$r_{TST}\cdot dt \;=\; k_{TST}\cdot[A]\cdot[B]\cdot dt \;=$$

$$[*]\cdot\frac{\displaystyle\int_0^{\infty}\frac{p\cdot dt}{\delta\cdot m^*}\cdot\exp\left(-\frac{p^2}{2\cdot m^*\cdot k_B\cdot T}\right)dp}{\displaystyle\int_0^{\infty}\exp\left(-\frac{p^2}{2\cdot m^*\cdot k_B\cdot T}\right)dp} =$$

$$\boxed{\frac{[*]\cdot dt\cdot \cancel{m^*}\cdot k_B\cdot T}{\delta\cdot\cancel{m^*}\cdot\sqrt{2\cdot\pi\cdot m^*\cdot k_B\cdot T}}}$$





P. Pechukas, Statistical Approximations in Collision Theory, *In* Dynamics of Molecular Collisions - Part B, W. Miller, ed. Springer 1976

Transition State Theory

- Collecting the relations in red boxes: $$\frac{[*]}{[A]\cdot[B]} = \frac{Q_*}{Q_A \cdot Q_B}$$

$$k_{TST} = \frac{[*]}{[A]\cdot[B]} \cdot \frac{k_B \cdot T}{\delta \cdot \sqrt{2 \cdot \pi \cdot m^* \cdot k_B \cdot T}}$$

$$Q_* = \frac{\delta}{h} \cdot Q^{\ddagger} \cdot \sqrt{2 \cdot \pi \cdot m^* \cdot k_B \cdot T}$$

... we end up with: $$\boxed{k_{TST} = \frac{Q^{\ddagger}}{Q_A \cdot Q_B} \cdot \frac{k_B \cdot T}{h}}$$

Usually, one encounters a slightly modified version:

- Fudge factor κ accounting for re-crossings
- Potential energy contribution taken out of the partition functions

$$\boxed{k_{TST} = \kappa \cdot \frac{k_B \cdot T}{h} \cdot \frac{q^{\ddagger}}{q_{reac}} \cdot \exp\left(-\frac{E^{\ddagger}}{k_B \cdot T}\right)}$$

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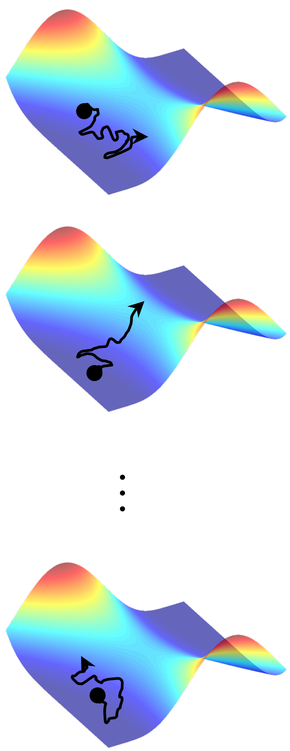
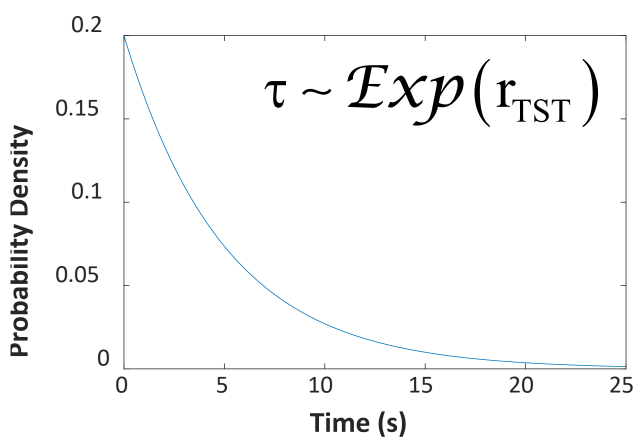
So What Does It All Mean?

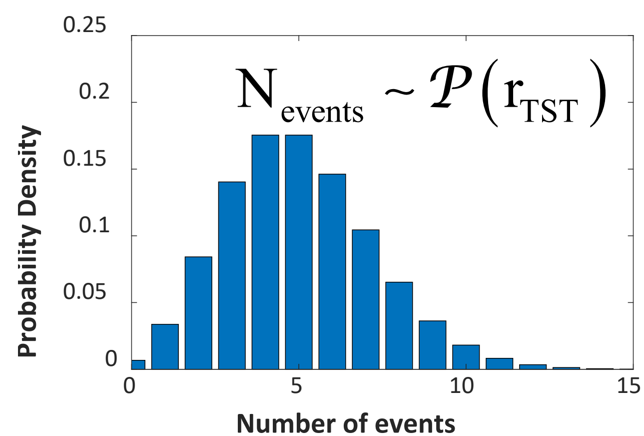
- $r_{TST} = k_{TST} \cdot [A] \cdot [B] \cdot dt$ = average number of transitions from reactants to products per unit time. But what about the statistics?



Ensemble

- **The system is memoryless** $\Rightarrow$
  - Waiting time for reaction events follows the exponential distribution with rate parameter r_{TST}
  - Number of events in given time interval follows the Poisson distribution with rate parameter r_{TST}





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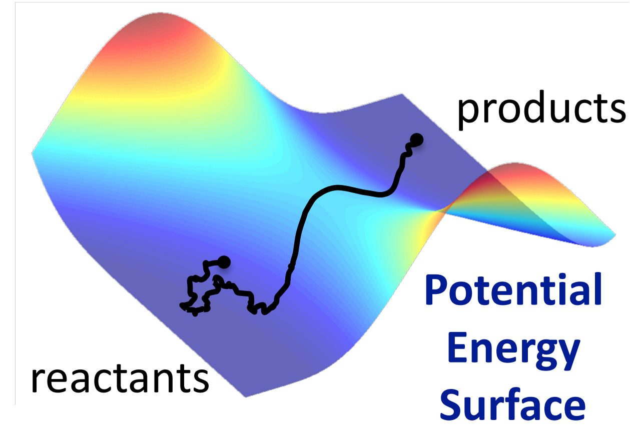
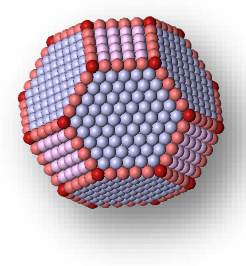
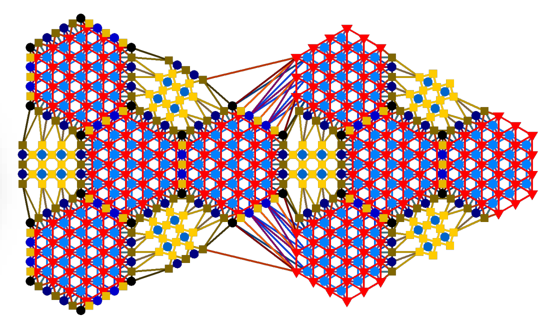
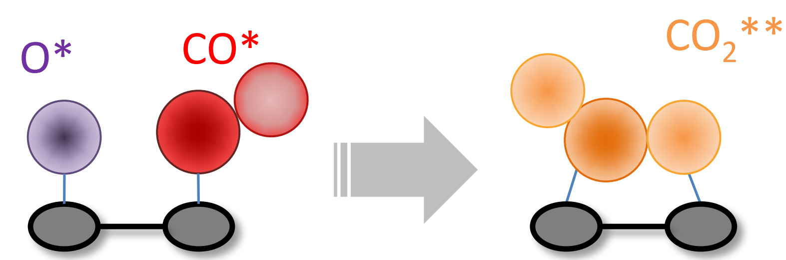


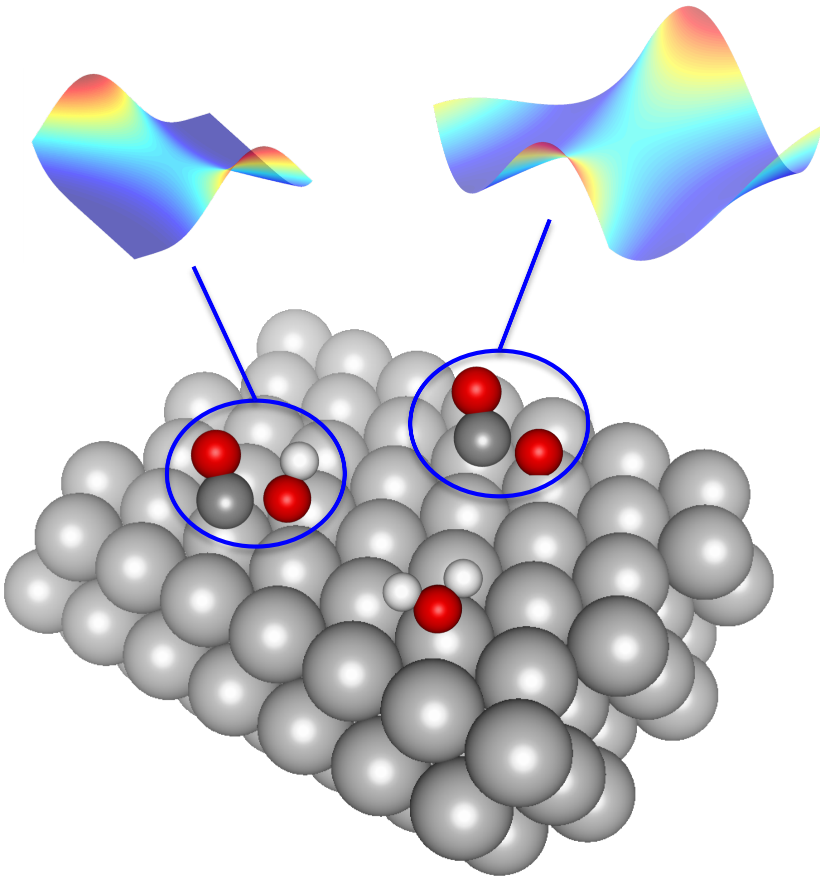






From One Reaction to Many…

- Many species on catalytic surface, many possible reaction types, each with its own rate constant:



$$\tau_1 \sim \mathcal{E}xp\left(r_{TST,1}\right)$$

$$\tau_2 \sim \mathcal{E}xp\left(r_{TST,2}\right)$$

$$\vdots$$

$$\tau_n \sim \mathcal{E}xp\left(r_{TST,n}\right)$$

Time of occurrence of next event:

$$\tau = \min_i\left(\tau_i\right) \sim \mathcal{E}xp\left(\sum_{i=1}^{n} r_{TST,i}\right)$$

Event to occur:

the one with the smallest time.

From One Reaction to Many…

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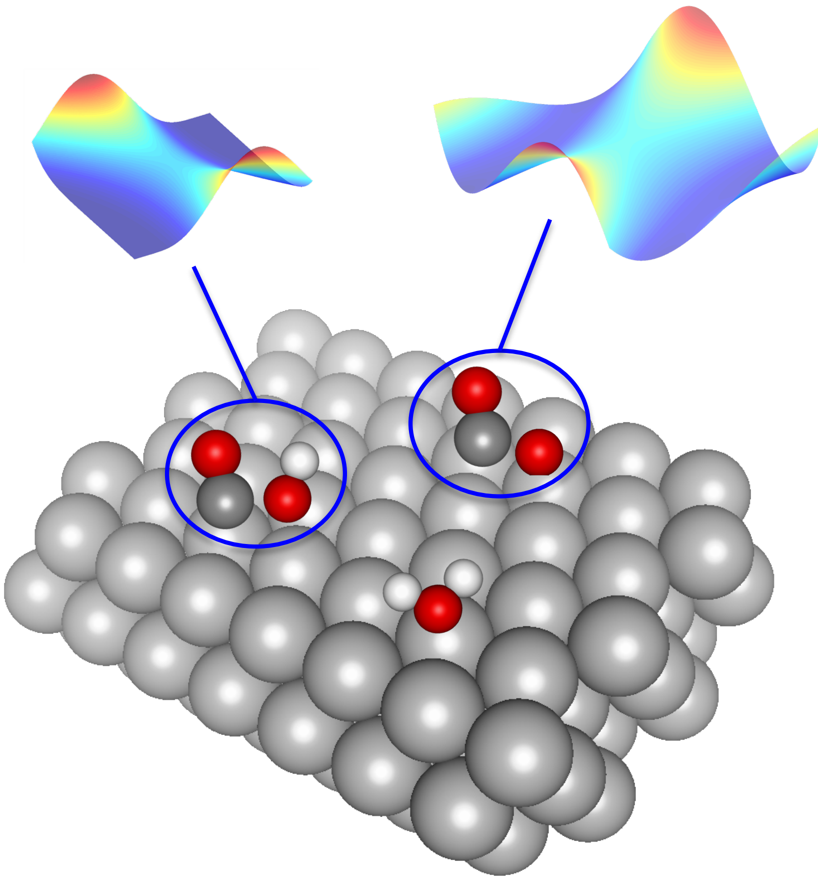


Time of occurrence of next event:

$$\tau = \min_i(\tau_i) \sim \mathcal{E}xp\left(\sum_{i=1}^{n} r_{TST,i}\right)$$

Event to occur:
the one with the smallest time.

$\Rightarrow$ we can simulate a sequence of lattice configurations and take samples

Equation governing the statistics of these configurations?

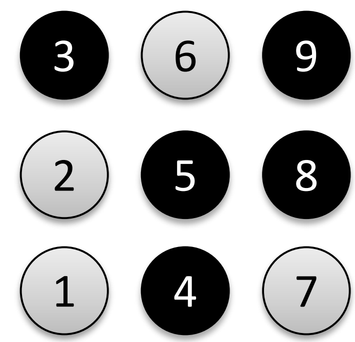
The Master Equation

Probability of configuration $\boldsymbol{\sigma}$

$$\frac{d\boxed{P(\boldsymbol{\sigma})}}{dt} = \sum_{\boldsymbol{\sigma}'}\left[\boxed{W_{\boldsymbol{\sigma}'\to\boldsymbol{\sigma}}\cdot P(\boldsymbol{\sigma}')} - \boxed{W_{\boldsymbol{\sigma}\to\boldsymbol{\sigma}'}\cdot P(\boldsymbol{\sigma})}\right]$$

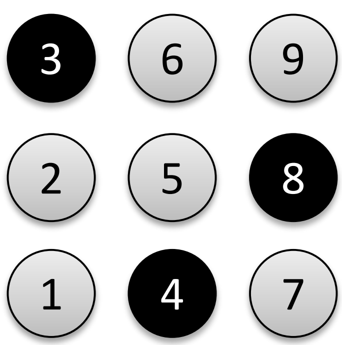
Probability efflux to other configurations $\boldsymbol{\sigma}'$

Probability influx from other configurations $\boldsymbol{\sigma}'$

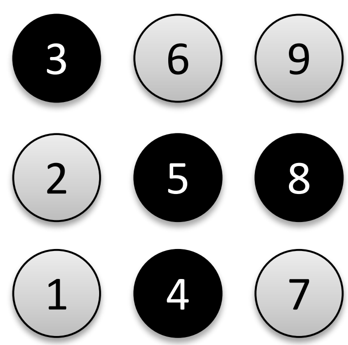


Adsorption on site 9

$$\boldsymbol{\sigma}' = (0,0,1,1,1,0,0,1,\mathbf{1})$$



Adsorption on site 5



$$\boldsymbol{\sigma}' = (0,0,1,1,\mathbf{0},0,0,1,0)$$

$$\boldsymbol{\sigma} = (0,0,1,1,1,0,0,1,0)$$

The Master Equation

Probability of configuration $\boldsymbol{\sigma}$

$$\frac{\boxed{dP(\boldsymbol{\sigma})}}{dt} = \sum_{\boldsymbol{\sigma}'} \left[\boxed{W_{\boldsymbol{\sigma}' \to \boldsymbol{\sigma}} \cdot P(\boldsymbol{\sigma}')} - \boxed{W_{\boldsymbol{\sigma} \to \boldsymbol{\sigma}'} \cdot P(\boldsymbol{\sigma})} \right]$$

Probability efflux to other configurations $\boldsymbol{\sigma}'$

Probability influx from other configurations $\boldsymbol{\sigma}'$

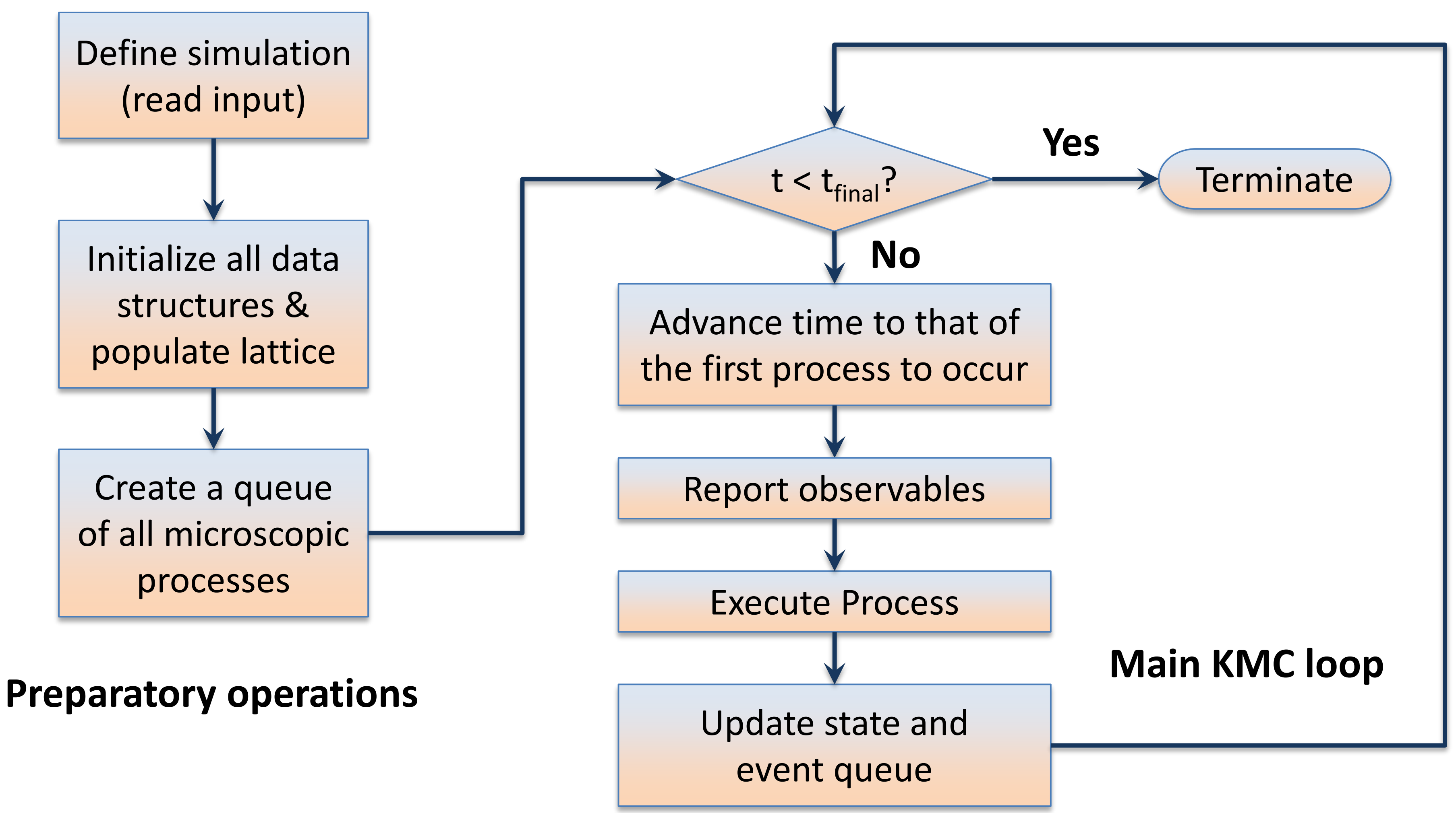
- Equation linear with respect to $P(\sigma)$ but **state space** often too large,

  e.g. for lattice gas $2^{N_{sites}} = 5.62 \times 10^{14}$ for $N_{sites} = 49$

✓ We simulate & sample stochastic trajectories (KMC method)

Jansen, A. P. J. (2012). An introduction to kinetic Monte Carlo simulations of surface reactions. Berlin, Springer-Verlag.
Darby, M. T., Piccinin, S. and M. Stamatakis (2016). Chapter 4: First principles-based kinetic Monte Carlo simulation in catalysis" in Kasai, H. and M. C. S. E. Escaño (Eds.), Physics of Surface, Interface and Cluster Catalysis, Bristol, UK: IOP Publishing.

KMC Algorithm Flowchart



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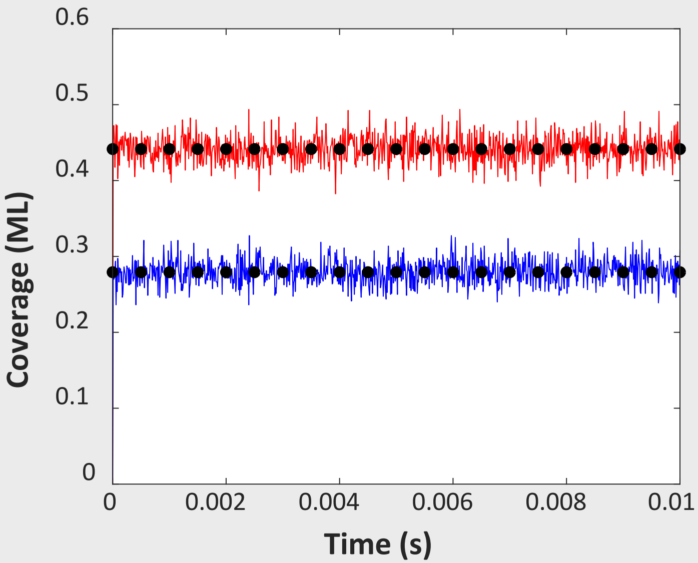
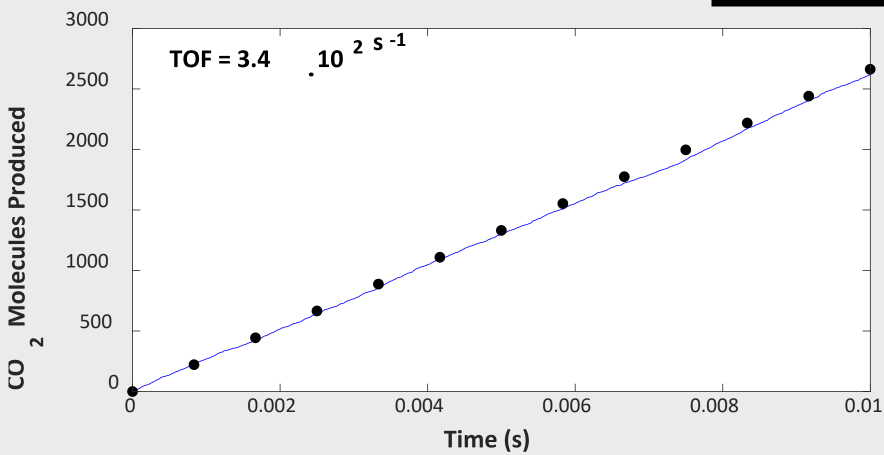
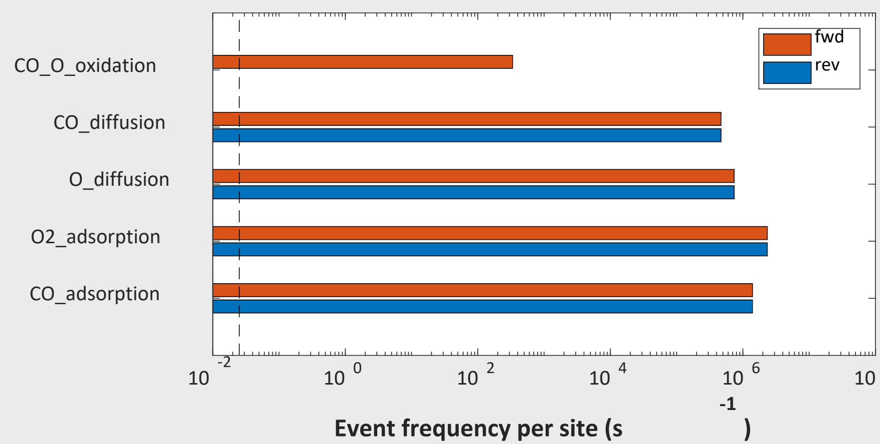
Typical KMC Output







✍ Homework: you are now at a position to be able to code a simple KMC program!

Try to set up a simple adsorption/desorption simulation and compare your results with the analytical expression from the Langmuir isotherm.

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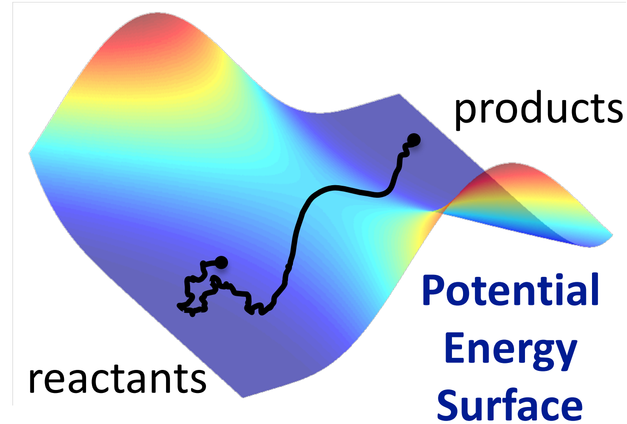
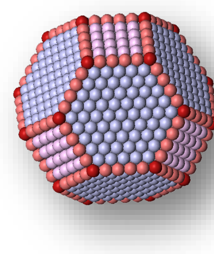
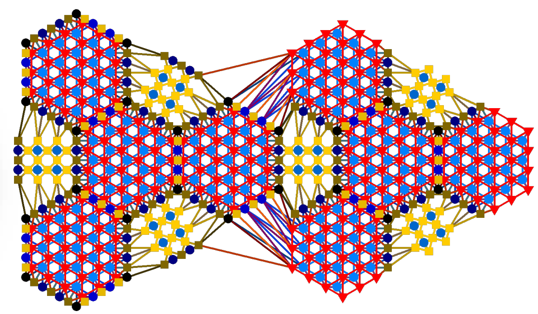
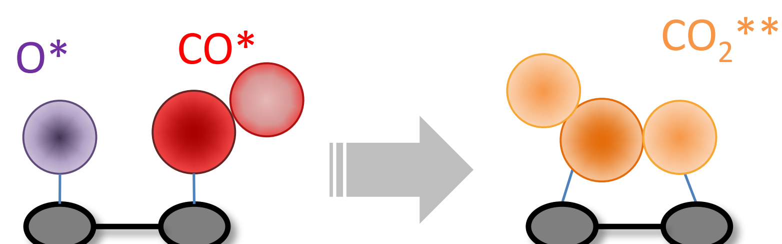


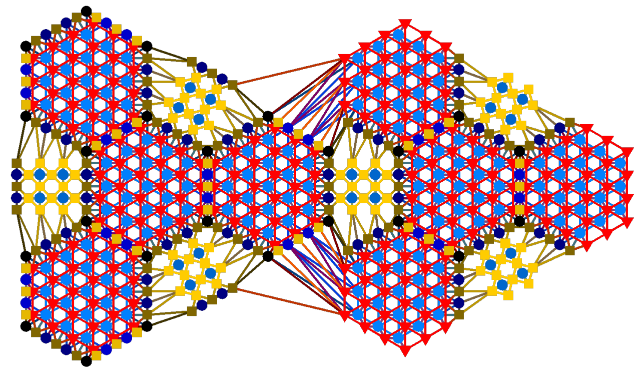




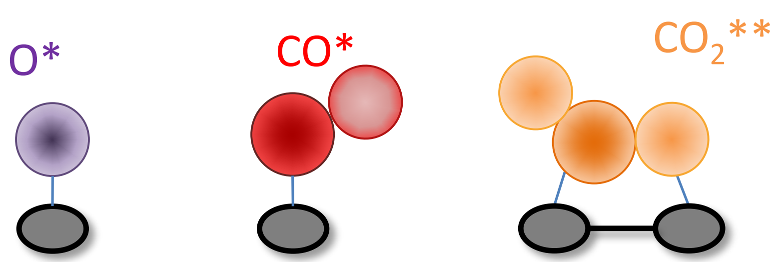


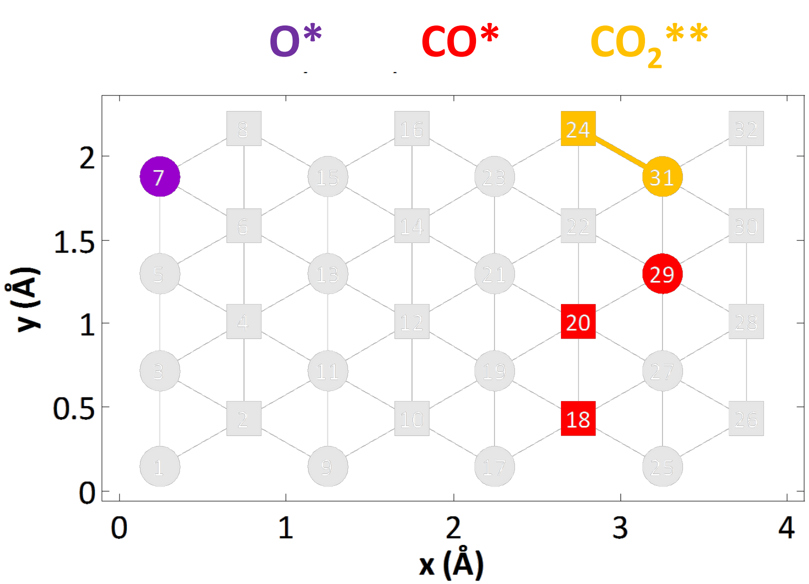
Graph-Theoretical KMC Approach

- Lattice represented as **graph**
  - Multiple site types
  - Arbitrary connectivity of sites



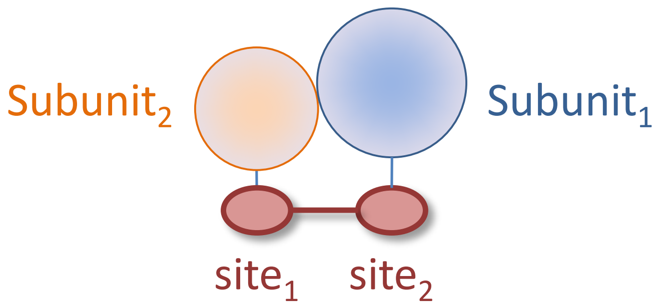
- State: molecular entity, species, and dentate for every site
  - **Multi-dentate** species allowed
  - **Orientation** explicitly captured





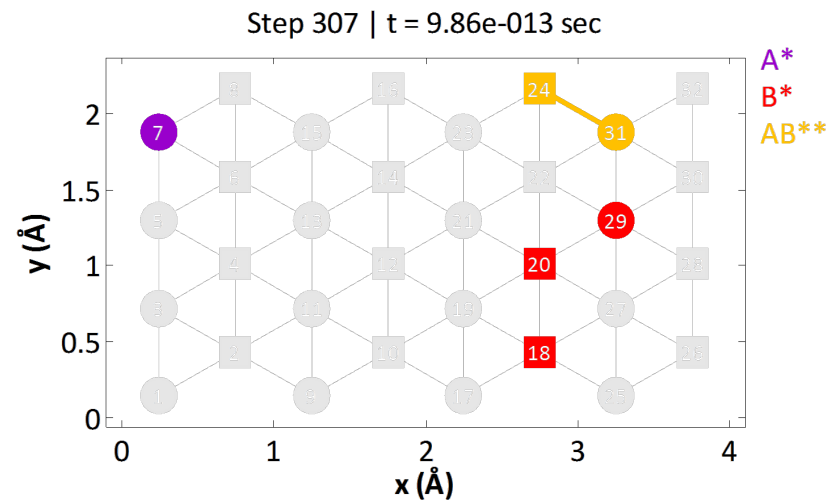
M. Stamatakis and D. G. Vlachos, J. Chem. Phys. 134(21): 214115 (2011).

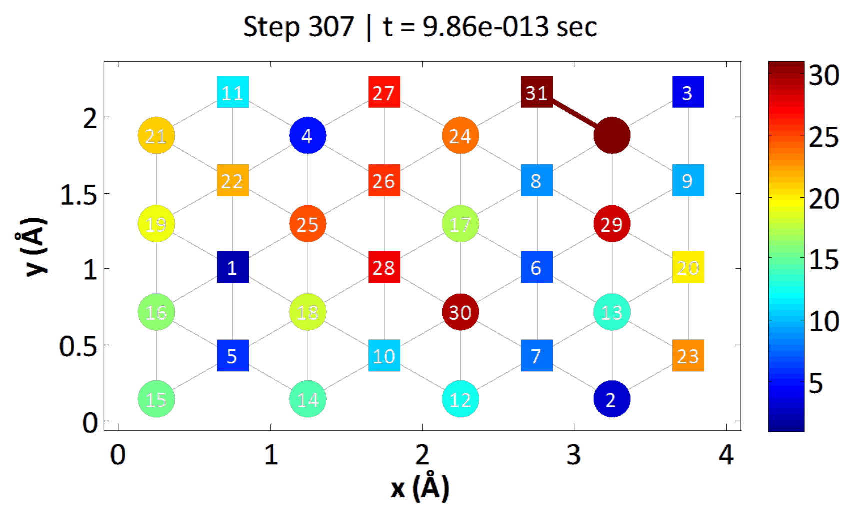
Lattice State Representation



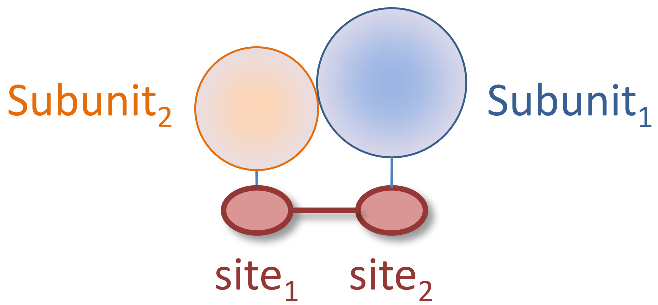
- **Multi-dentate** species modeled (bind to more than one sites)
- Lattice represented as **graph**
- State specifies species & dentation ∀ site

Site	Entity	Species	Dentate
1	15	0	1
2	5	0	1
3	16	0	1
⋮	⋮	⋮	⋮
7	21	1	1
18	7	2	1
⋮	⋮	⋮	⋮
24	31	3	1
⋮	⋮	⋮	⋮
31	31	3	2
32	3	0	1



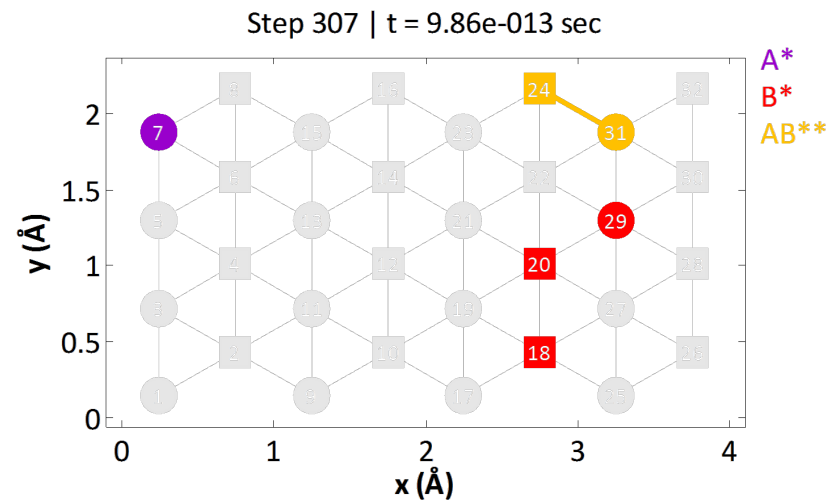


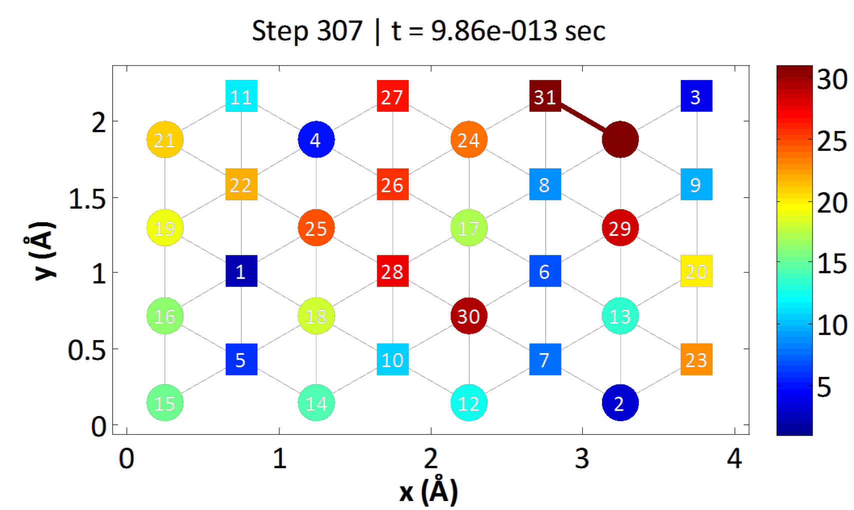
Lattice State Representation



- **Multi-dentate** species modeled (bind to more than one sites)
- Lattice represented as **graph**
- State specifies species & dentation ∀ site

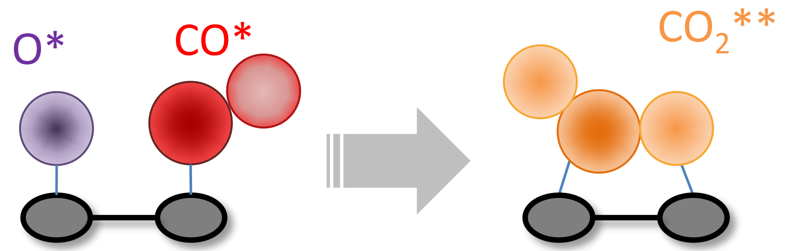
Entity	Species	Sites
1	0	4
⋮	⋮	⋮
7	2	18
⋮	⋮	⋮
21	1	7
31	3	24,31
⋮	⋮	⋮

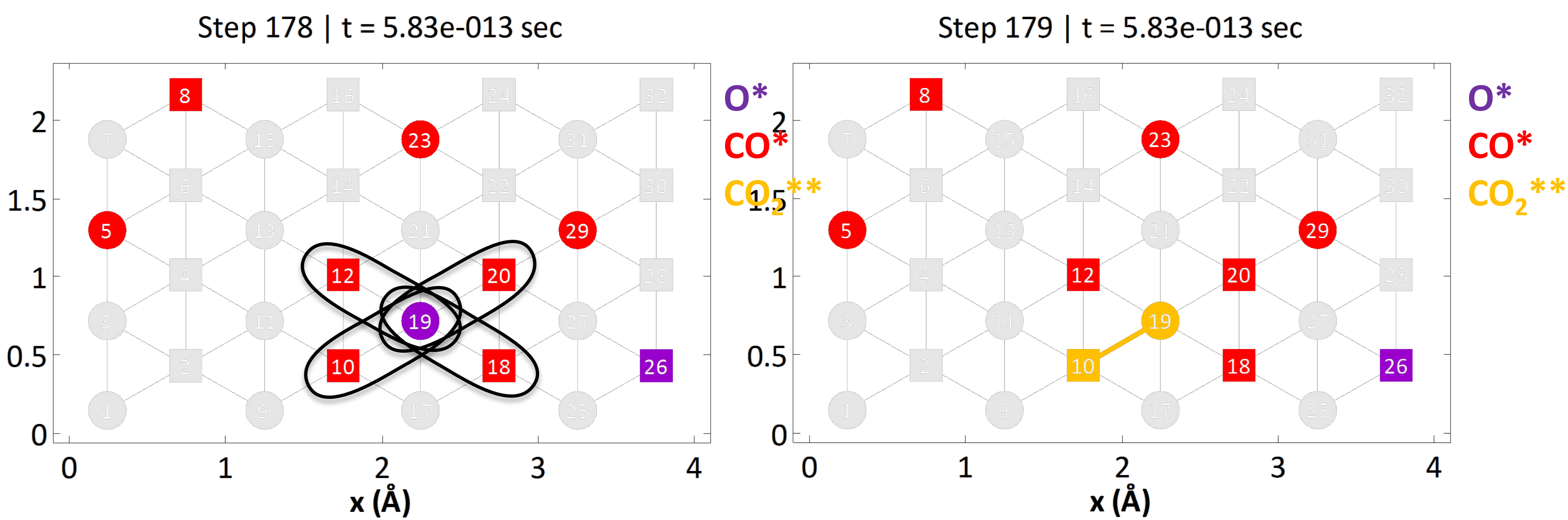




Elementary Step Representation

- Elementary steps → connected graphs
- **Subgraph isomorphism** used to
  - identify possible elementary steps
  - map them to lattice processes



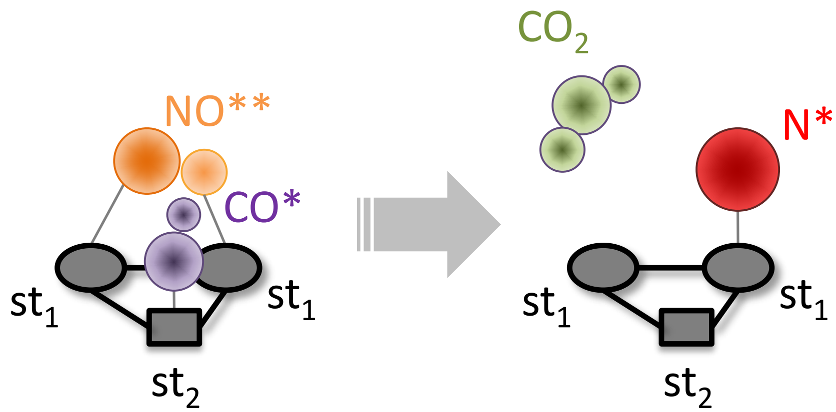


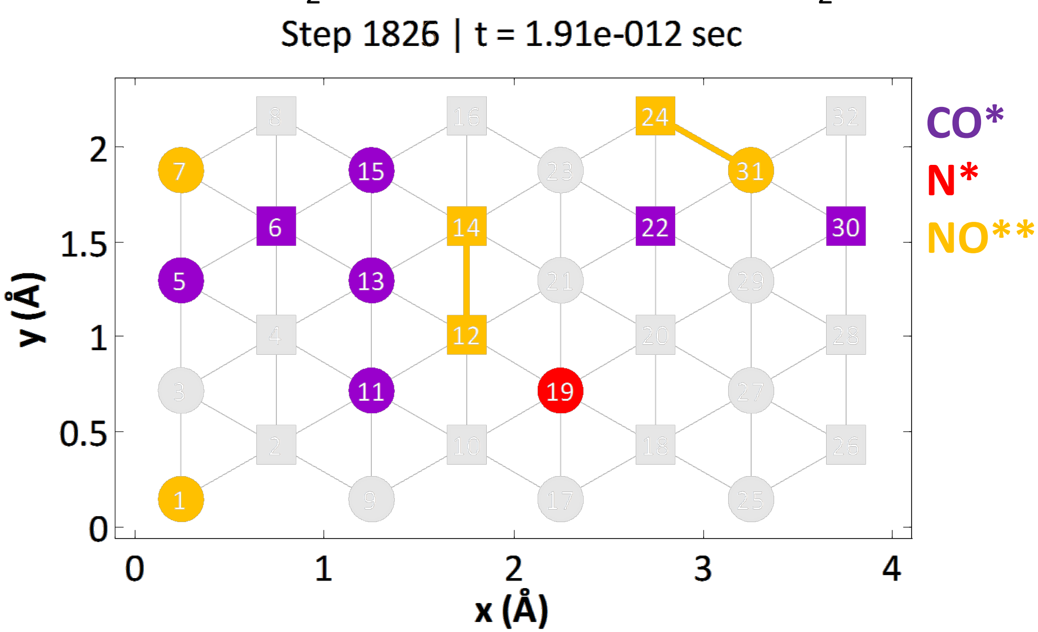
M. Stamatakis and D. G. Vlachos, J. Chem. Phys. 134(21): 214115 (2011).

Solving the Subgraph Isomorphism

- **Subraph isomorphism**:
  - Create all permutations of N_{sub} out of N_L lattice sites
  - Check each permutation
- **Optimizations**:
  - Check permutations while constructing (Ullmann 1976)
  - Consider only sites within certain distance from entity

  ⇒ **localized pattern search**





M. Stamatakis and D. G. Vlachos, J. Chem. Phys. 134(21): 214115 (2011).

Lattice Process Lists

- Given lattice state, each **lattice process** fully specified by
  - Type of elementary step
  - Site mapping:

Process	Elem. Step	Sites
1	1	4
2	2	5,6
3	1	5
4	1	6
5	3	2,3,1
⋮	⋮	⋮

Lattice Process ↔ Elementary Step

Which sites are involved in process P_i?

Entity	#Procs	Processes
1	5	34,12,65,74,10
2	3	12,2,1
3	1	5
4	2	6,8
5	3	43,30,1
⋮	⋮	⋮

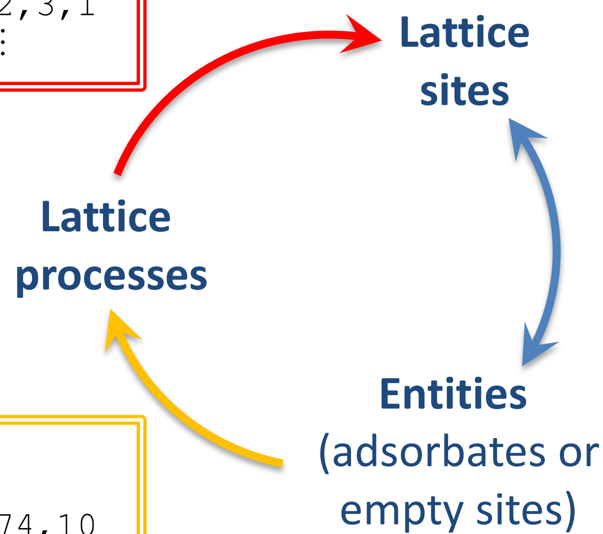
Participation Array

Which process entity E_i participates in?

M. Stamatakis and D. G. Vlachos, J. Chem. Phys. 134(21): 214115 (2011).

KMC Book-keeping

Process	Elem. Step	Sites
1	1	4
2	2	5,6
3	1	5
4	1	6
5	3	2,3,1
⋮	⋮	⋮



Site	Entity	Species	Dentate
1	15	0	1
2	5	0	1
3	16	0	1
⋮	⋮	⋮	⋮
7	21	1	1
18	7	2	1
⋮	⋮	⋮	⋮
24	31	3	1
⋮	⋮	⋮	⋮
31	31	3	2
32	3	0	1

Entity	Species	Sites
1	0	4
⋮	⋮	⋮
7	2	18
⋮	⋮	⋮
21	1	7
31	3	24,31
⋮	⋮	⋮

Entity	#Procs	Processes
1	5	34,12,65,74,10
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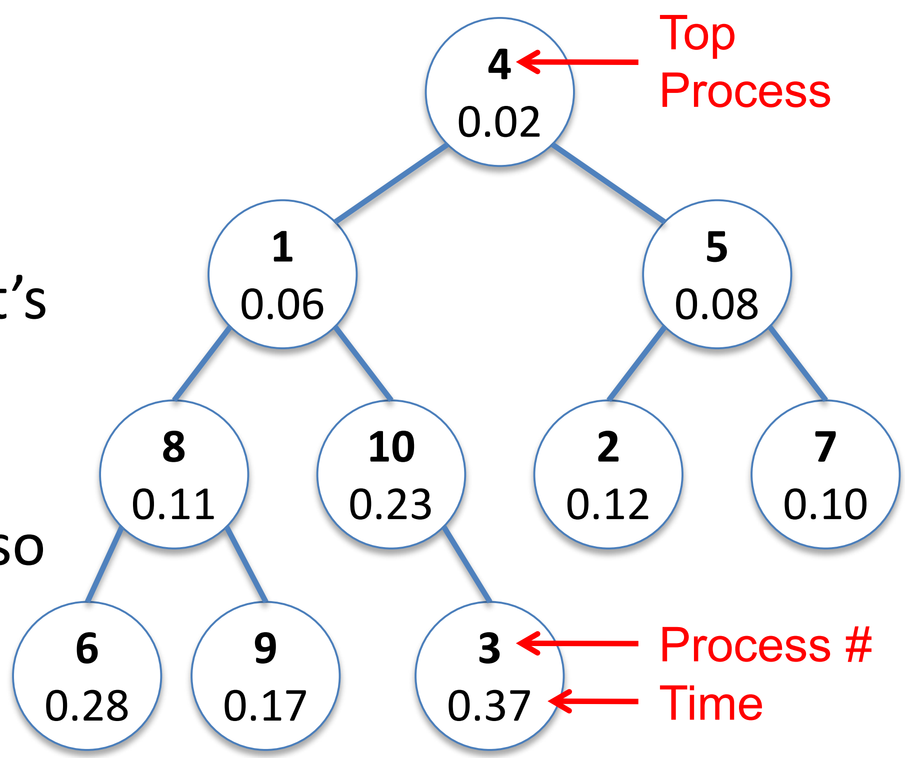
5	3	43,30,1
⋮	⋮	⋮

M. Stamatakis and D. G. Vlachos, J. Chem. Phys. 134(21): 214115 (2011).

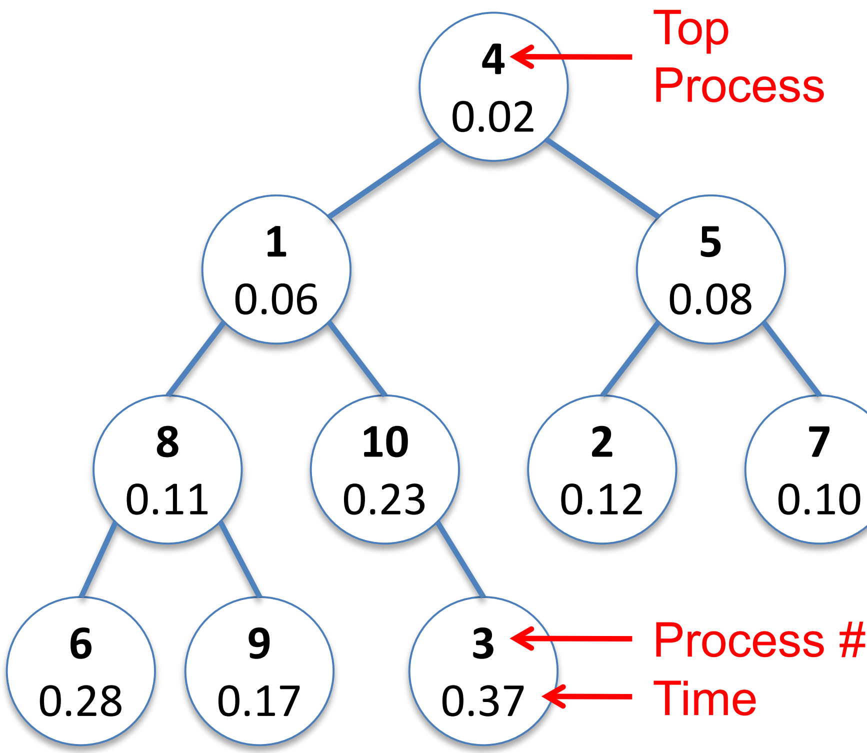
Selecting the Next Event to Happen

- Heap structure:
  - Partially ordered binary tree
  - Each node has **priority** over **all its children nodes**
  - Priority determined by event's execution time
  - **Insert**, **update**, **remove** operations reorder the tree so that the **heap property is always satisfied**
  - Next KMC event always found in the top node



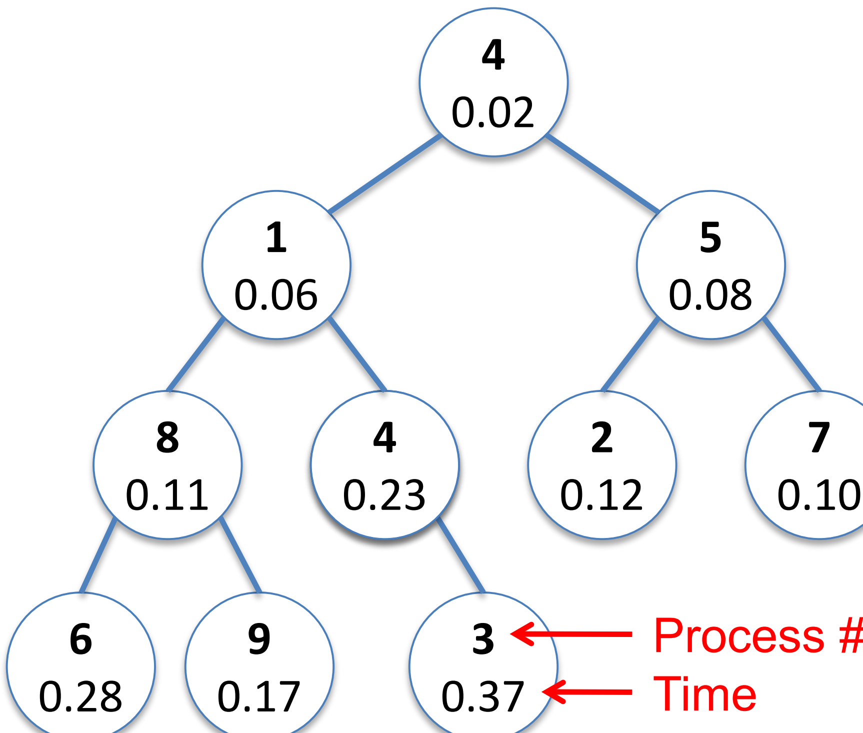
Use of Heap Arrays for Queue Construction

- **Heap structures** for the queue of processes to be executed
- Addition, removal, update of a process $\rightarrow$ **automatic sorting**



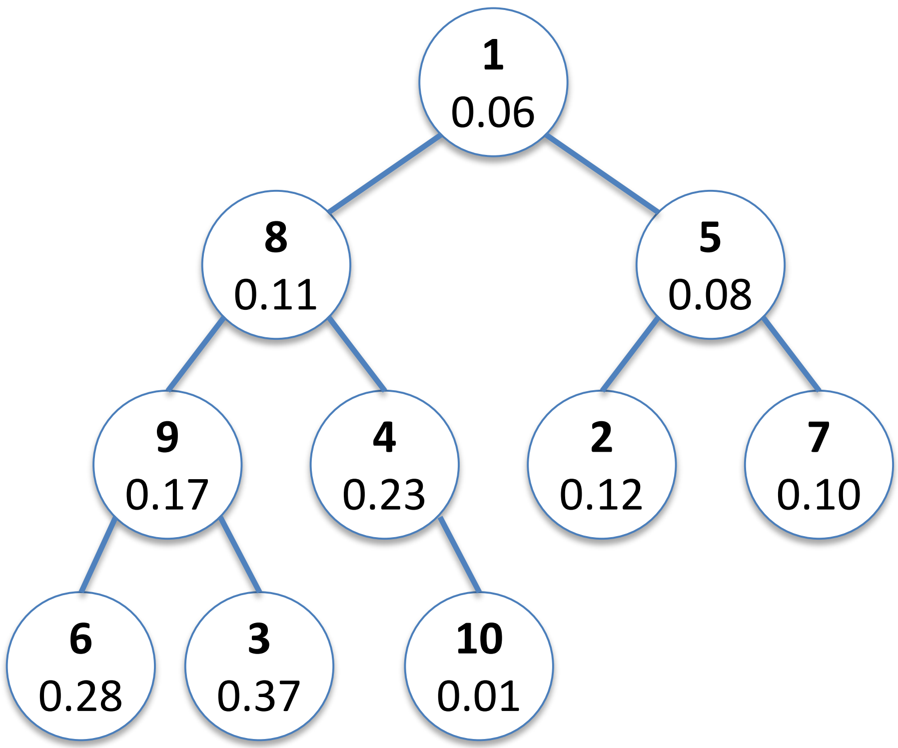
Heap Removal Operation

- Assume that process 4 just occurred
- Removal of that process from the heap:



Heap Addition Operation

- Assume we just found another feasible lattice process
- Addition of the 10th process:



Heap Addition Operation

- Assume we just found another feasible lattice process
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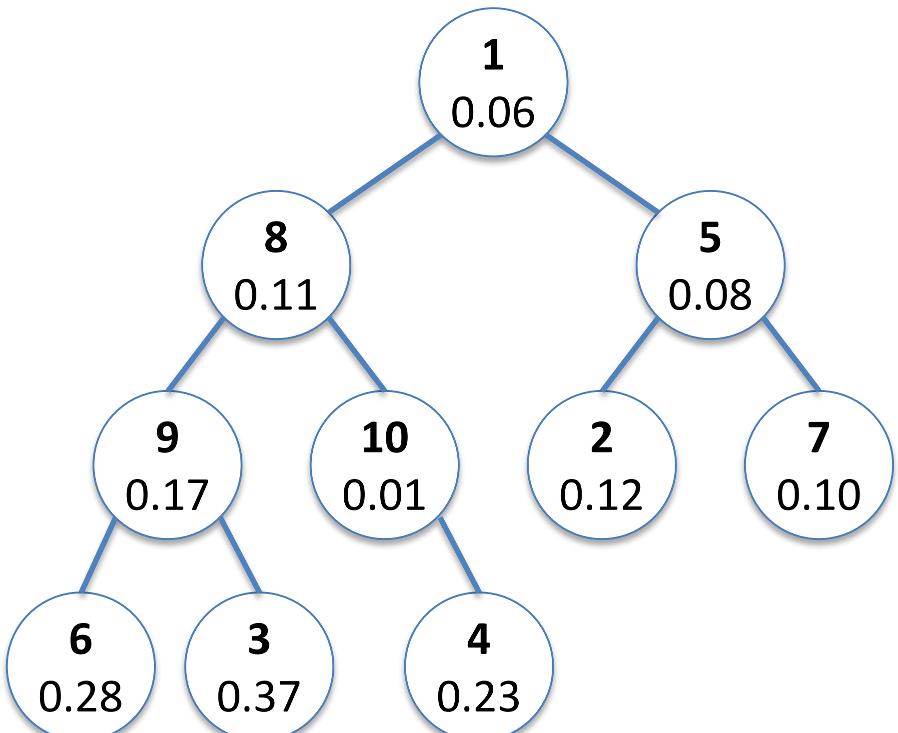
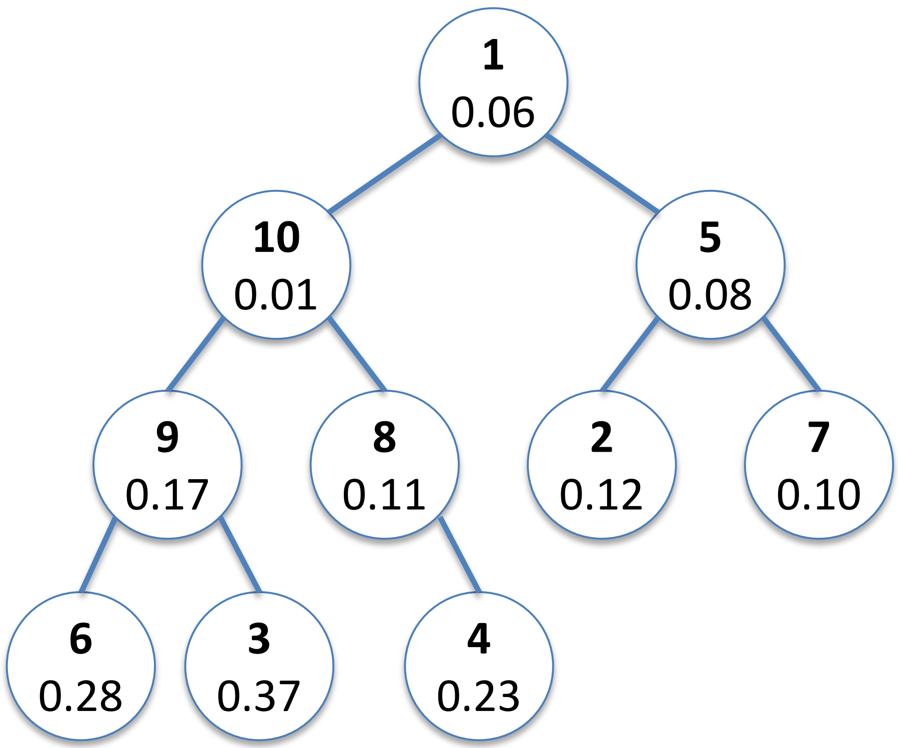


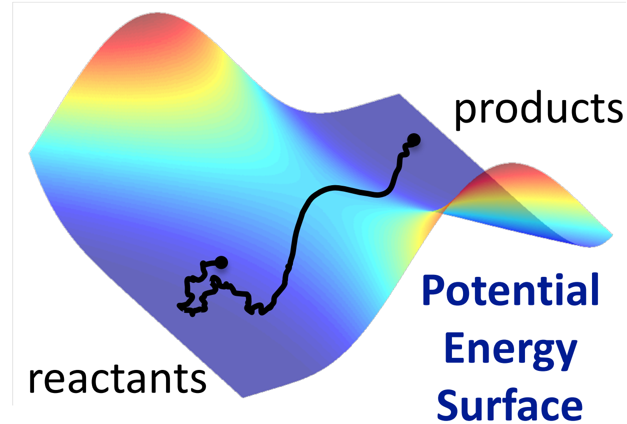
Heap Addition Operation

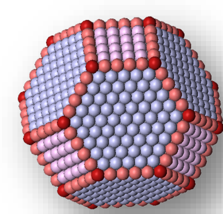
- Assume we just found another feasible lattice process
- Addition of the 10^{th} process:

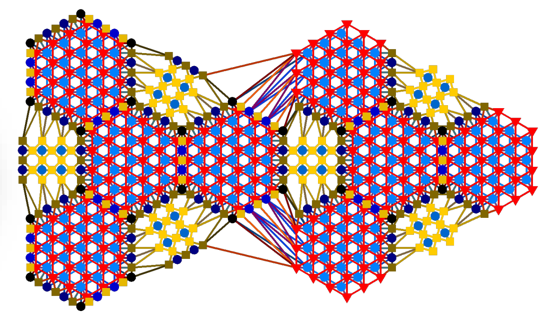


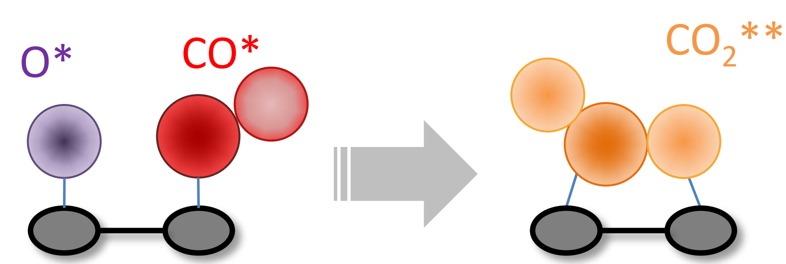
Outline

- Atomistic/Molecular level
  - Calculating rates for elementary events (transition state theory)
- Mesoscopic level
  - Simulating reactions on spatially extended systems
- **Accurate modelling of catalytic surface reactions**
  - Complex materials (lattices)
  - Complicated reactions
  - **Coverage effects**



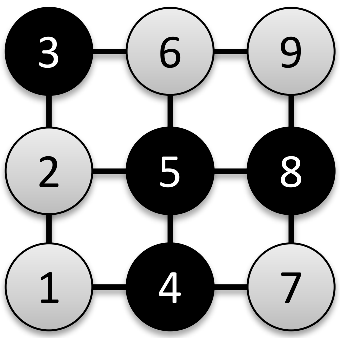






Non-ideal Adlayers

- Adsorbates on the surface exert attractive/repulsive interactions
  - of the adlayer is not (necessarily) equal to the sum of adsorption energies, *e.g.*:



$$E_{tot} = 4\cdot E(\bullet) + \underbrace{2\cdot E(\bullet\!-\!\bullet) + 2\cdot E(\bullet\cdots\bullet) + \ldots}_{\text{Interaction energies (2-body and many-body)}}$$

Single body terms (adsorption energies)

Interaction energies (2-body and many-body)

- In the general case: cluster expansion

$$\mathcal{H}(\boldsymbol{\sigma}) = \sum_{k=1}^{N_C} \frac{\boxed{\mathrm{ECI}_k}}{\boxed{\mathrm{GM}_k}} \cdot \boxed{\mathrm{NCE}_k(\boldsymbol{\sigma})}$$

ECI: Effective cluster interaction

NCE: Number of instances of interactions pattern

GM: Graph multiplicity

Patterns represented as graphs, detected using same ideas as for reactions…

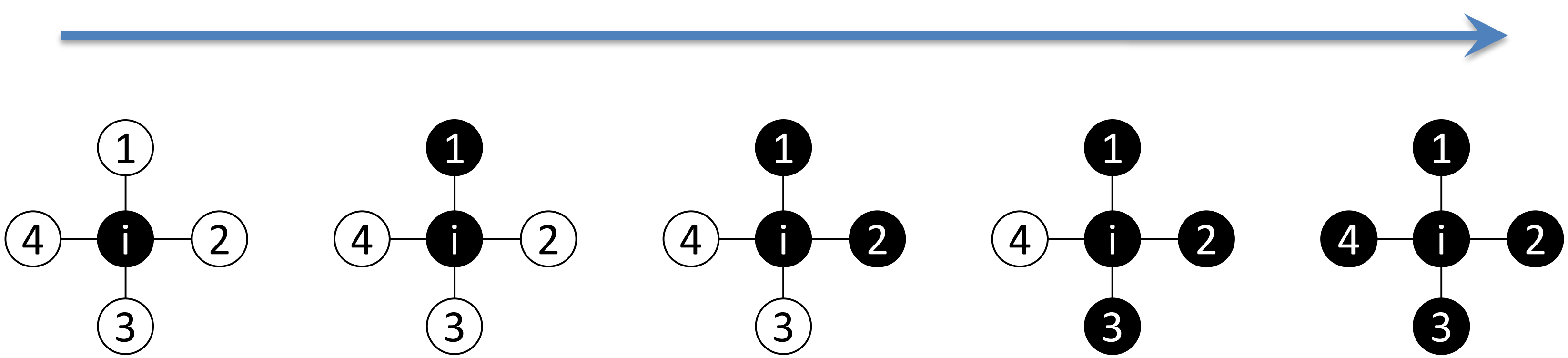
J. Nielsen, M. d'Avezac, J. Hetherington and M. Stamatakis, J. Chem. Phys. 139 (22), 224706 (2013).

Modelling Coverage Effects

- Attractive or repulsive interactions affecting rate, *e.g.*

$$W_{des,i} = A_{des} \cdot \exp\left(-\frac{E_a - J_{int} \cdot \sum_{j \in \mathcal{N}_i} \sigma_j}{k_B \cdot T} \right) \cdot \sigma_i$$

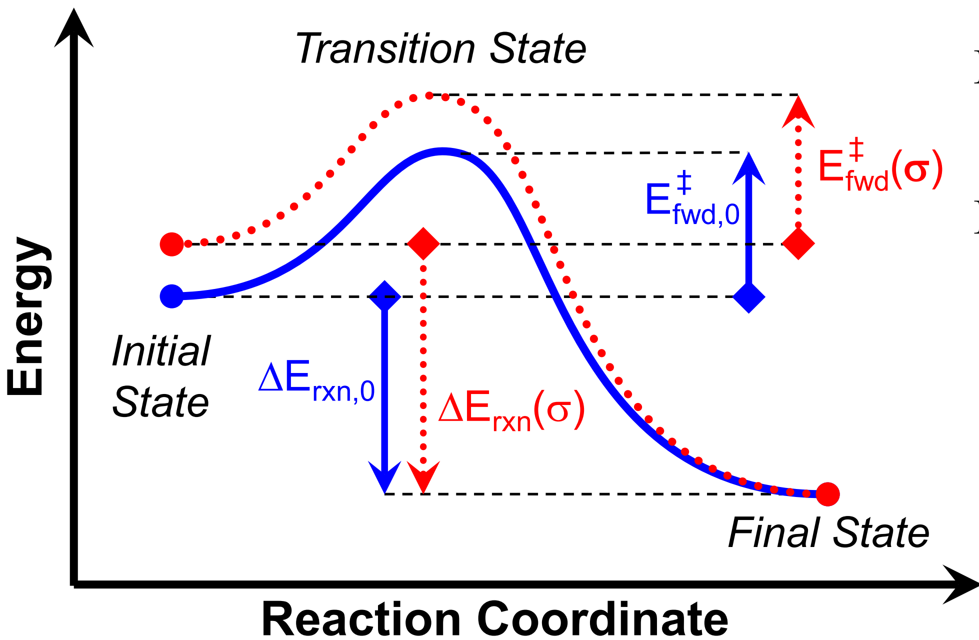
Rate increases for repulsive interactions ($J_{int} > 0$)



Treating the general case?

J. Nielsen, M. d'Avezac, J. Hetherington and M. Stamatakis, J. Chem. Phys. 139 (22), 224706 (2013).

Brønsted-Evans-Polanyi Relations



$$E^{\ddagger}_{fwd}(\boldsymbol{\sigma}) = E^{\ddagger}_{fwd,0} + \omega \cdot \left(\Delta E_{rxn}(\boldsymbol{\sigma}) - \Delta E_{rxn,0}\right)$$

$$E^{\ddagger}_{rev}(\boldsymbol{\sigma}) = E^{\ddagger}_{rev,0} - (1-\omega) \cdot \left(\Delta E_{rxn}(\boldsymbol{\sigma}) - \Delta E_{rxn,0}\right)$$

$$E^{\ddagger}_{rev,0} = E^{\ddagger}_{fwd,0} - \Delta E_{rxn,0}$$

$$\Rightarrow \Delta E_{rxn}(\boldsymbol{\sigma}) = E^{\ddagger}_{fwd}(\boldsymbol{\sigma}) - E^{\ddagger}_{rev}(\boldsymbol{\sigma})$$

... as expected (micro-reversibility)

- Linear correlation between activation and reaction energy
- Captures effect of local reaction environment on rate

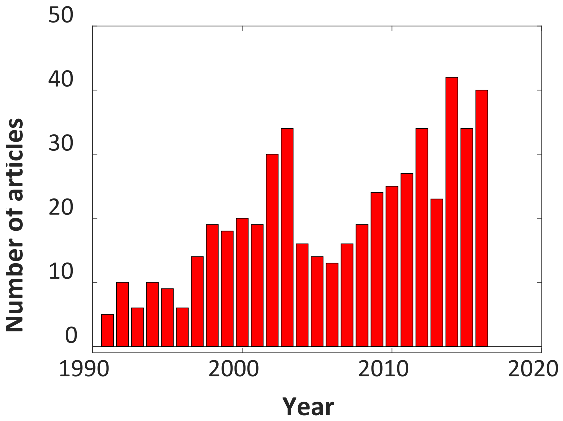
J. Nielsen, M. d'Avezac, J. Hetherington and M. Stamatakis, J. Chem. Phys. 139 (22), 224706 (2013).

Putting It All Together: Algorithm Outline

- Initialize all data structures & populate lattice
- Create a heap of all microscopic processes
- While $t < t_{final}$
  - Advance time to that of the top process
  - Execute corresponding process:
    - – Remove reactants from lattice, and associated processes and energetics
    - – Add products into lattice, add new energetic interactions
  - Update event queue:
    - – Add to heap all processes in which newly added products can participate
    - – Update processes of existing processes if needed (energetic interactions)
- Repeat

Take Home Messages

- Kinetic Monte-Carlo (KMC) simulation:
  – Versatile framework applicable to adsorption/desorption, reaction, diffusion (and other) processes
  – Attracting growing interest in the last few years



Number of articles published per year containing the keywords "kinetic Monte Carlo" and "catalys" (data from Web of Science)*

- KMC provides unique insight, by bridging
  – molecular scale processes (micro) &
  – observable phenomena (meso, macro)
  – having a dynamic component…