

Kinetic Monte Carlo Simulations of Surface Reactions

PHAS0076:
TYC Materials Modelling
Academic Year 2018-2019
Dr Michail Stamatakis

Why Do Kinetic Modelling in Catalysis and Surface Science?

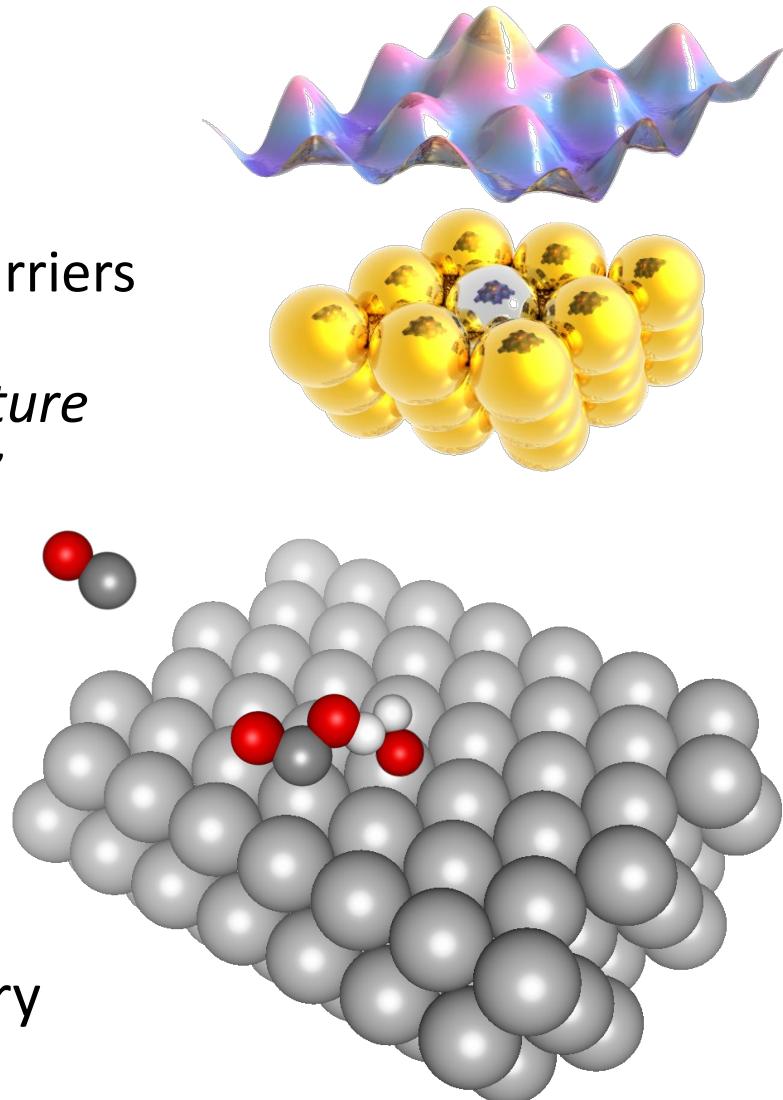
- **DFT Calculations in Catalysis:**
 - ✓ Electronic structure of materials
 - ✓ Stability of intermediates
 - ✓ Chemical pathways and energy barriers

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

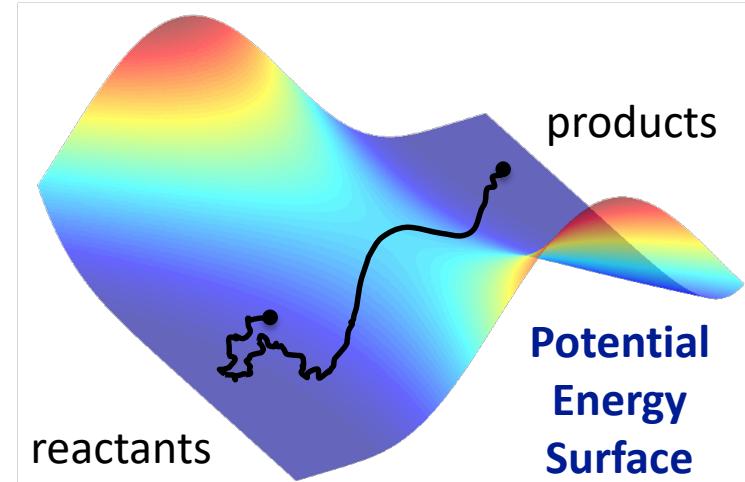
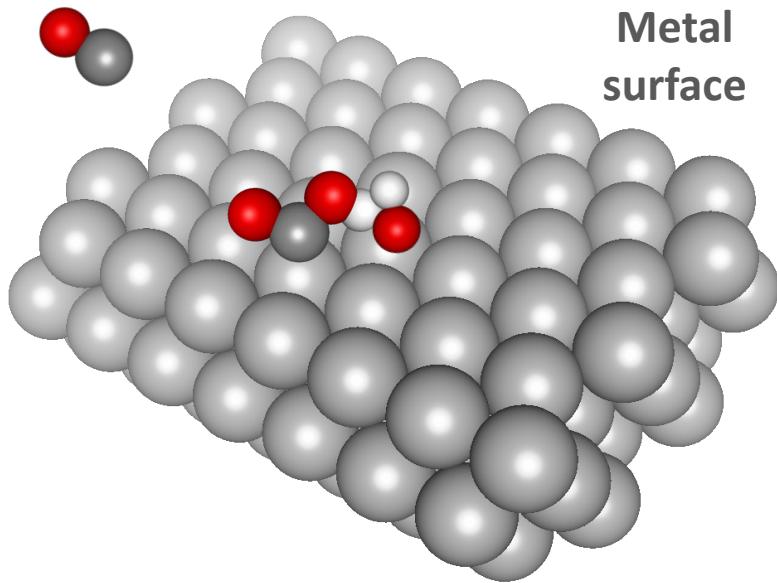
- Parallel or competing pathways?
- Temperature and pressure effects?
- Coverage effects on reaction rates?



Kinetic modelling necessary



The Kinetic Monte Carlo Approach

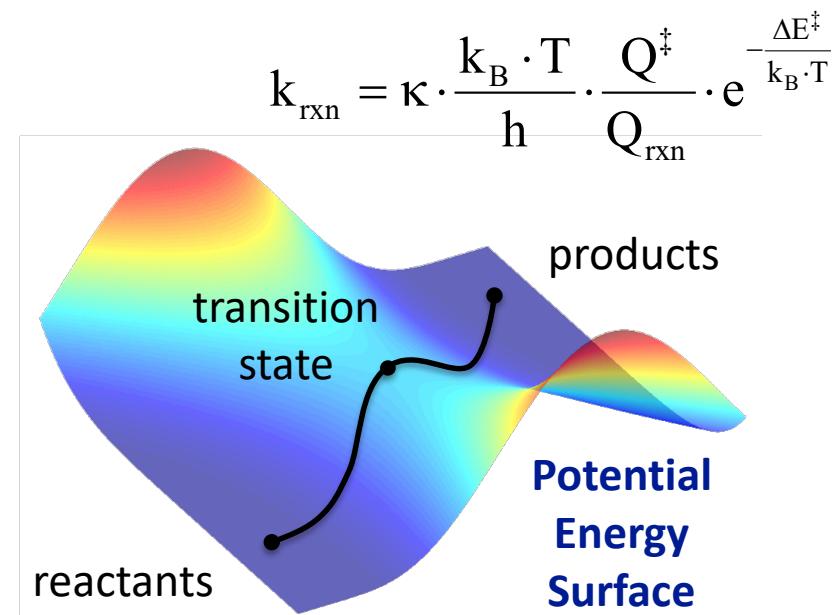
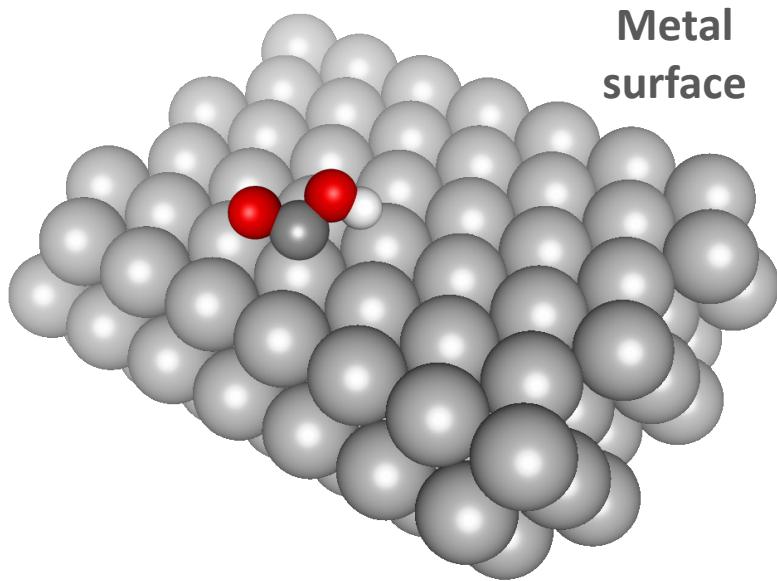


- Instead of simulating dynamics, KMC¹ focuses on rare events
- Simulates reactions much faster than Molecular Dynamics
- Incorporates spatial information contrary to micro-kinetic models²

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



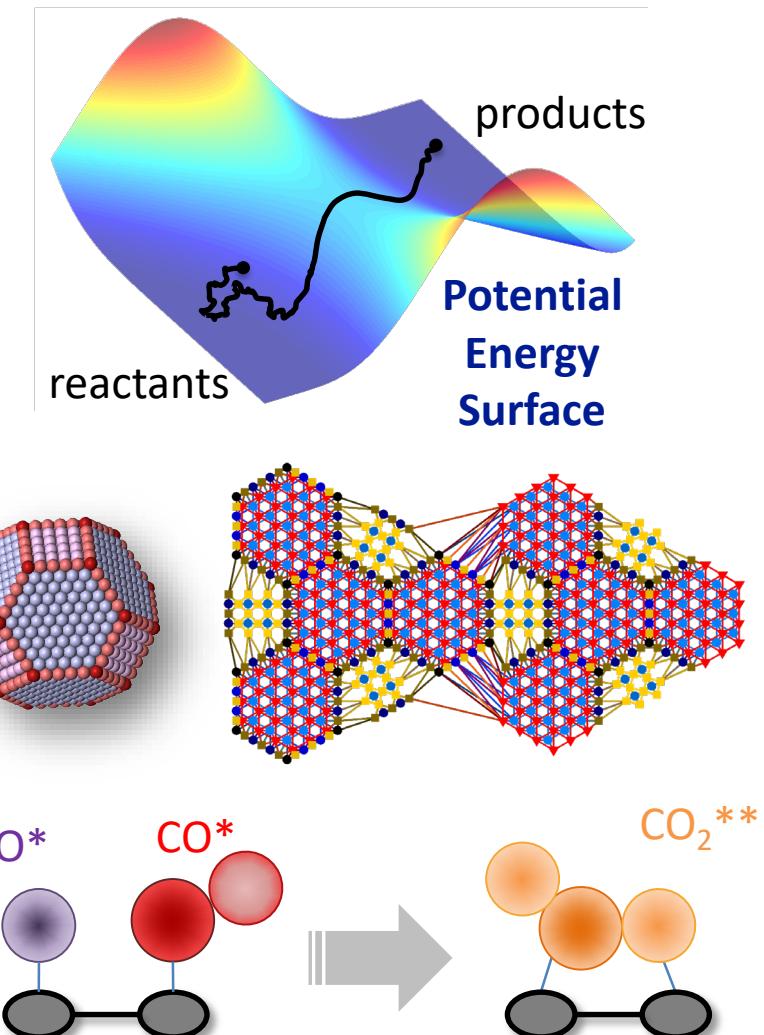
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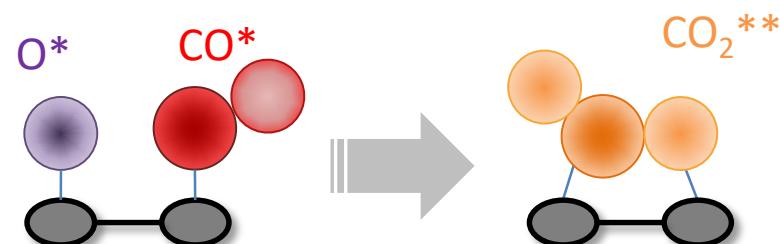
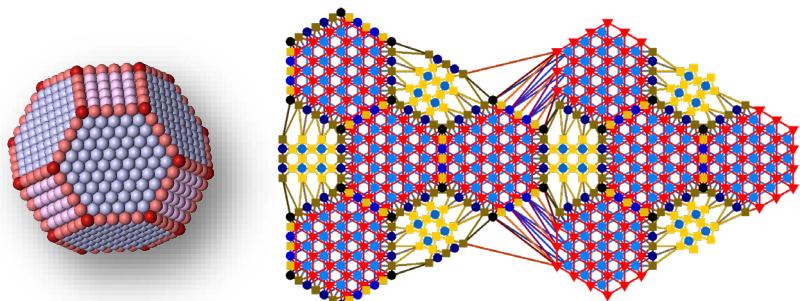
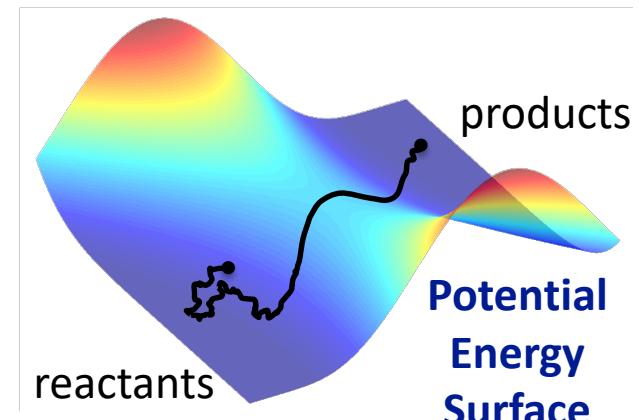
Outline

- 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



Outline

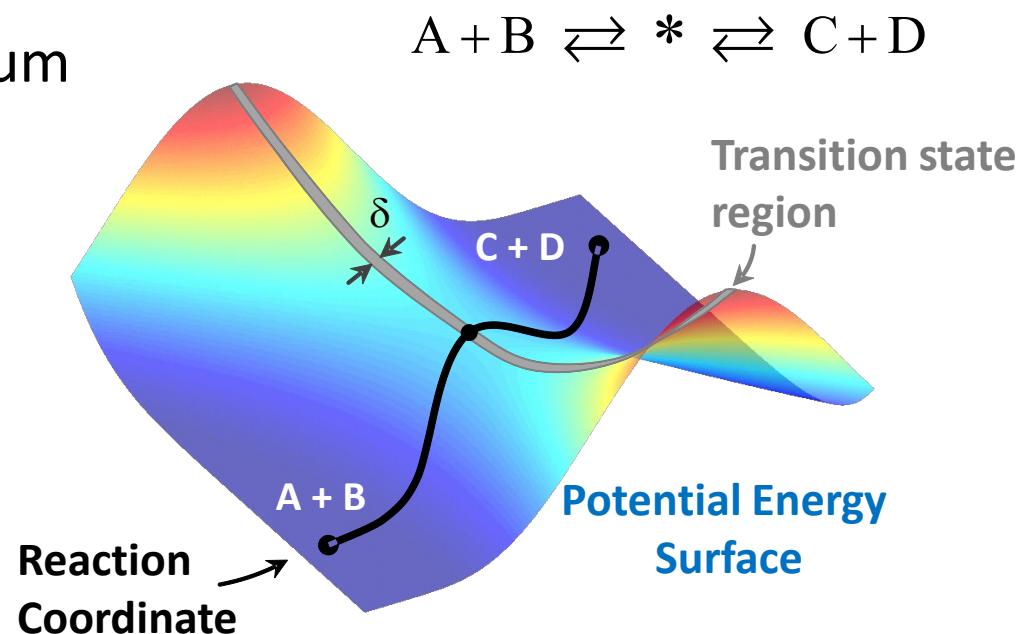
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Transition State Theory

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

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



$$Q_A = \frac{1}{h^{3 \cdot N_A}} \cdot \int \exp\left(-\frac{\mathcal{H}_A}{k_B \cdot T}\right) d\Gamma_A$$

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

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

$$\text{where } N = N_A + N_B$$

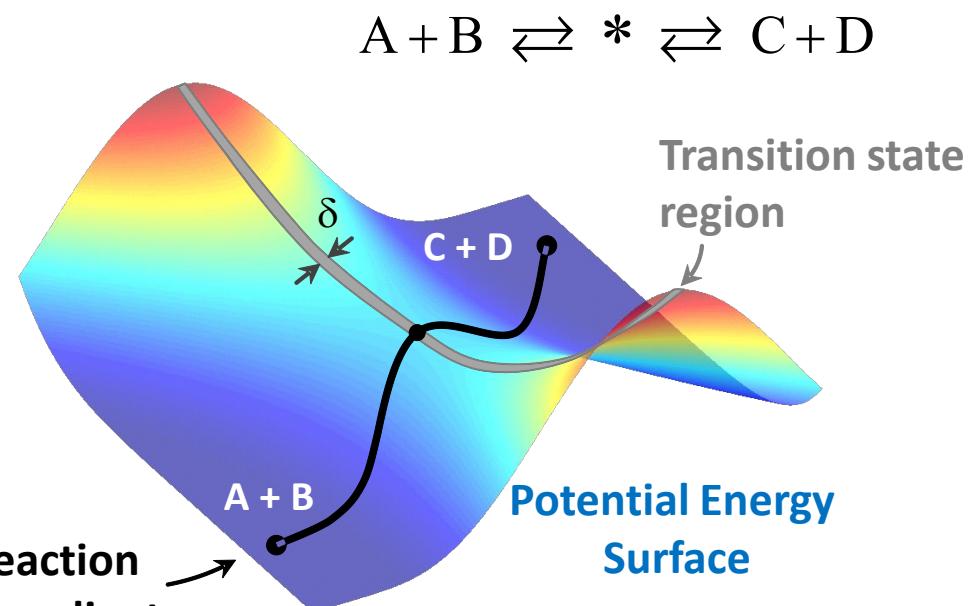
Transition State Theory

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

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

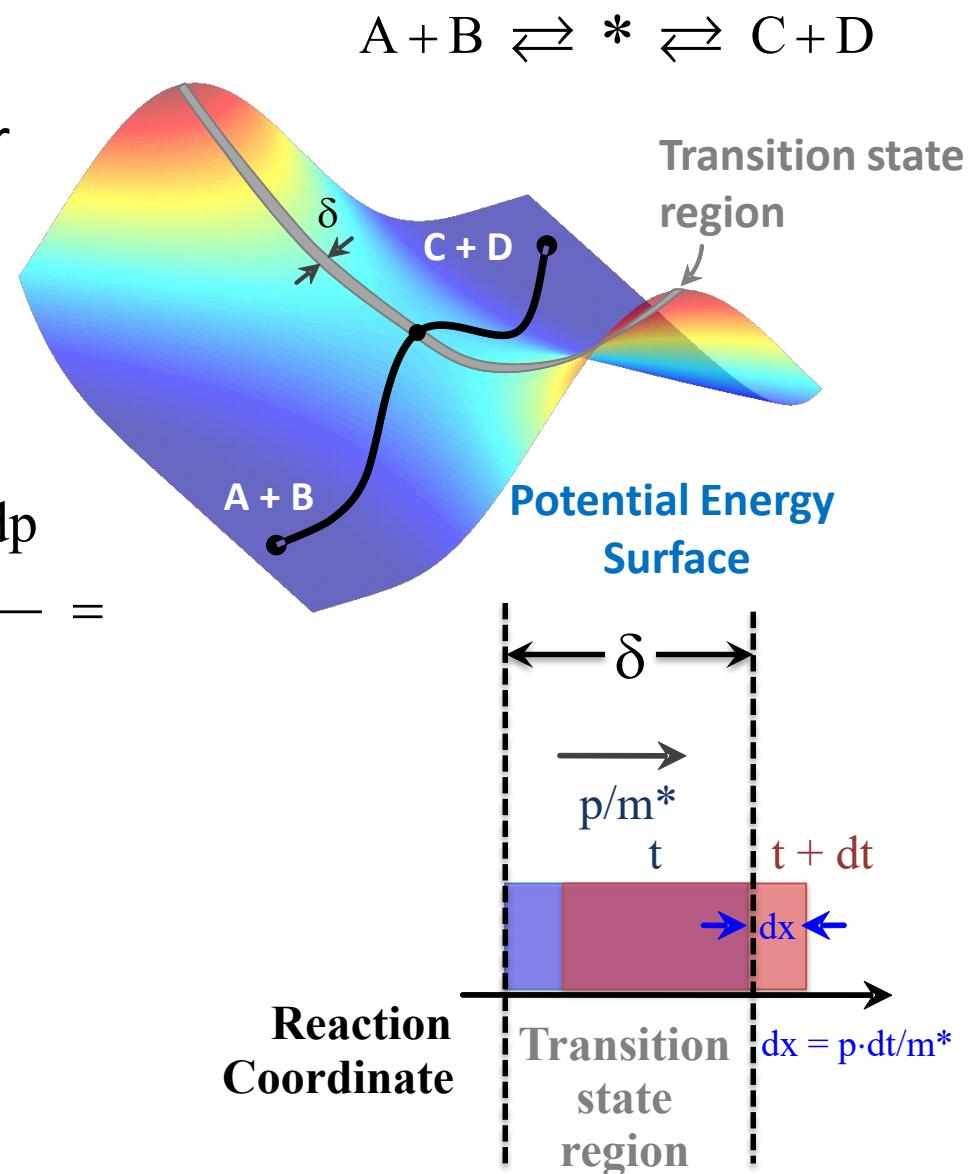
Transition State Theory

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

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

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

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



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:

$$k_{TST} = \frac{Q^\ddagger}{Q_A \cdot Q_B} \cdot \frac{k_B \cdot T}{h}$$

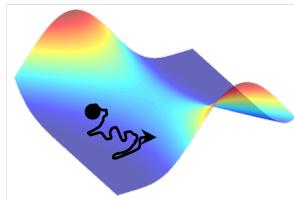
Usually, one encounters a slightly modified version:

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

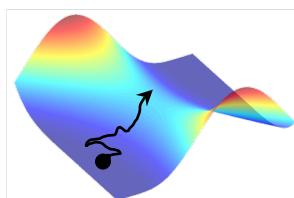
$$k_{TST} = \kappa \cdot \frac{k_B \cdot T}{h} \cdot \frac{q^\ddagger}{q_{\text{reac}}} \cdot \exp\left(-\frac{E^\ddagger}{k_B \cdot T}\right)$$

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?

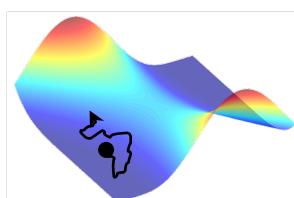


- **The system is memoryless \Rightarrow**

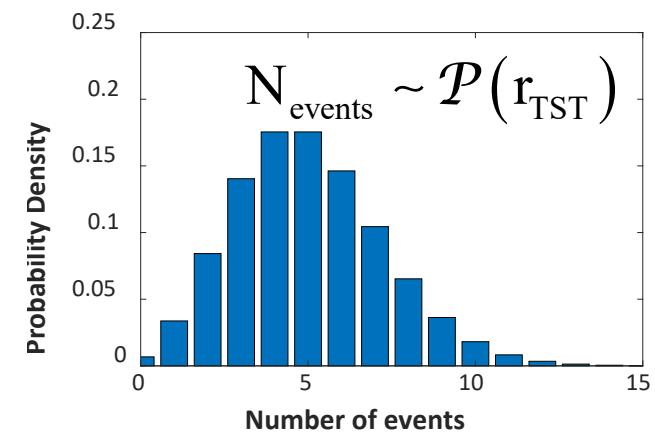
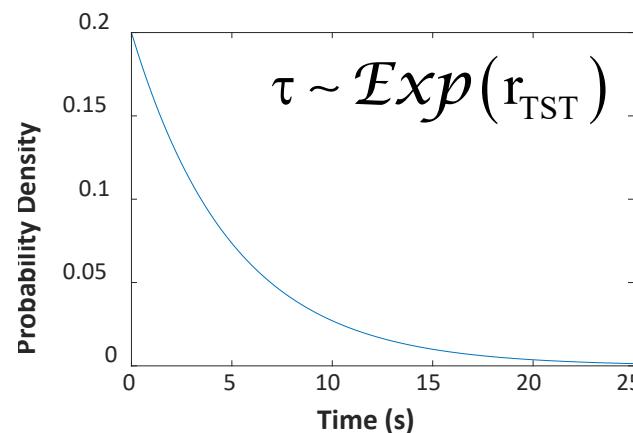


- Waiting time for reaction events follows the exponential distribution with rate parameter r_{TST}
- Number of events in given time interval follows the Poisson distribution with rate parameter r_{TST}

⋮



Ensemble

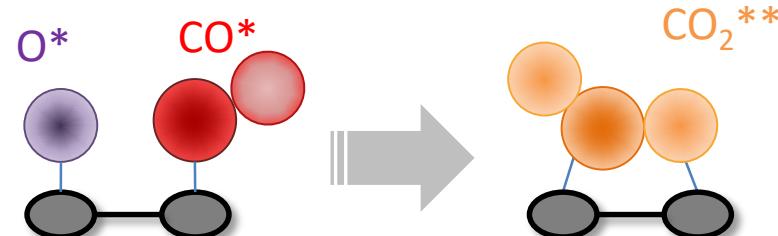
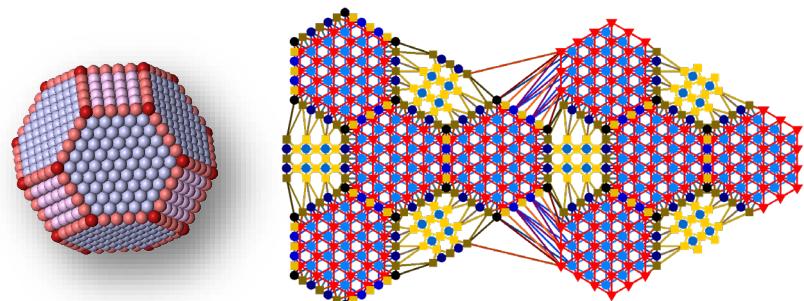
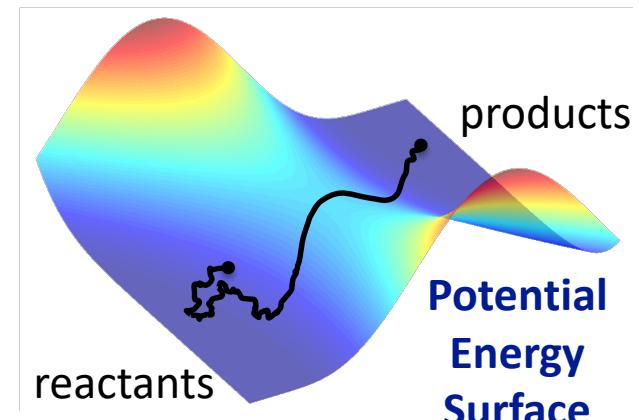


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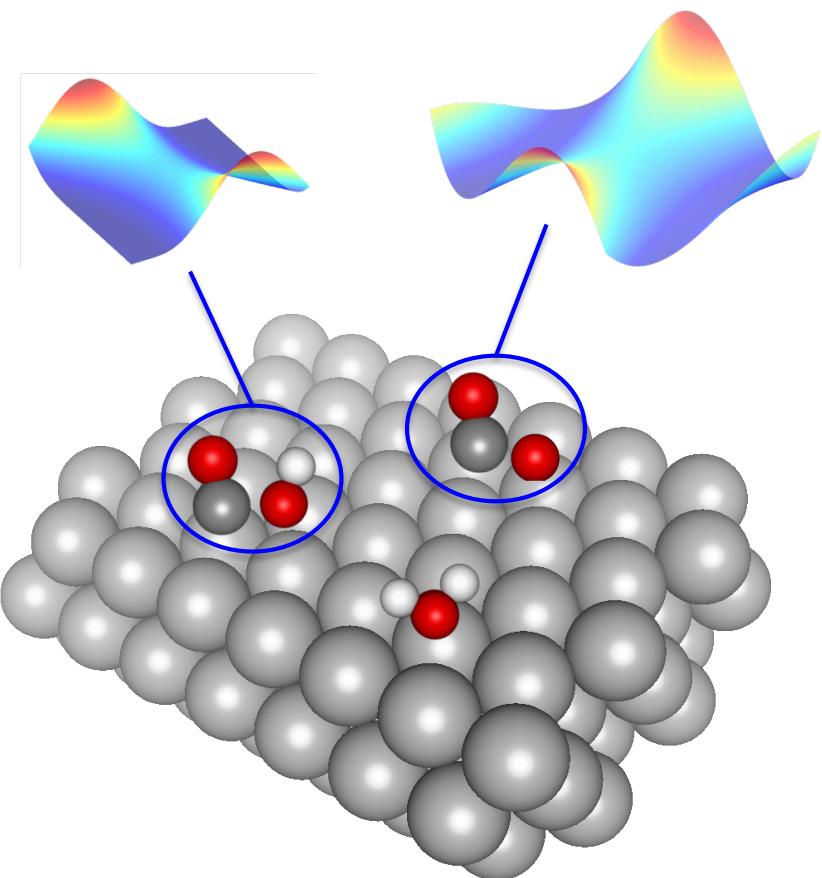
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From One Reaction to Many...

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



$$\tau_1 \sim \text{Exp}(r_{\text{TST},1})$$

$$\tau_2 \sim \text{Exp}(r_{\text{TST},2})$$

⋮

$$\tau_n \sim \text{Exp}(r_{\text{TST},n})$$

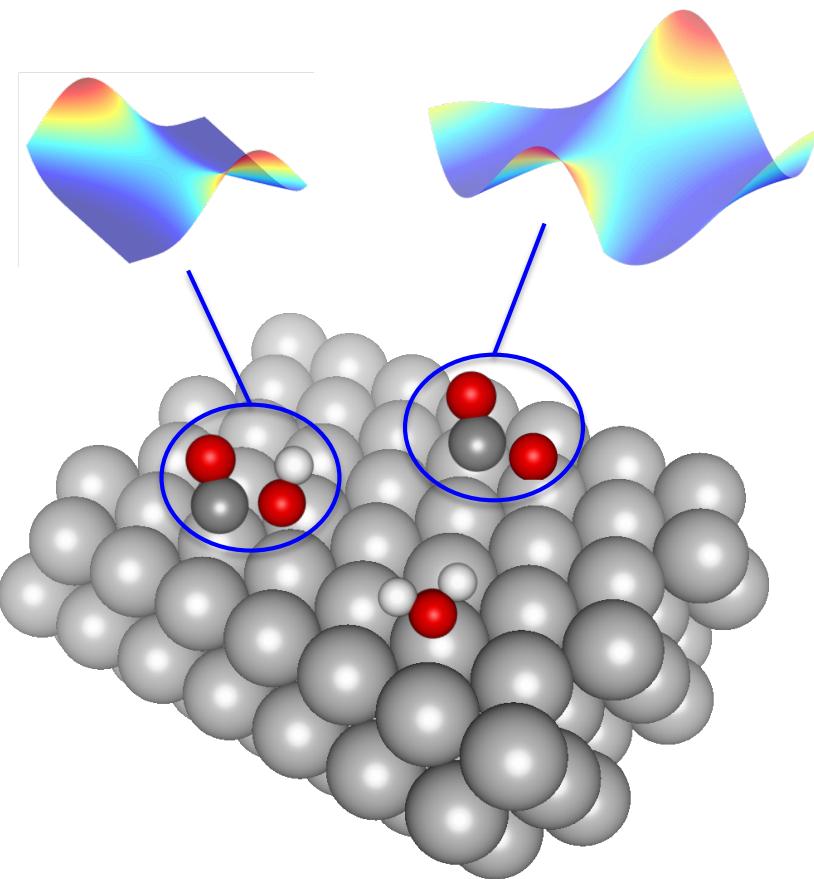
Time of occurrence of next event:

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

**Event to occur:
the one with the smallest time.**

From One Reaction to Many...

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



Time of occurrence of next event:

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

Event to occur:
the one with the smallest time.

⇒ we can simulate a sequence of lattice configurations and take samples

**Equation governing the statistics
of these configurations?**

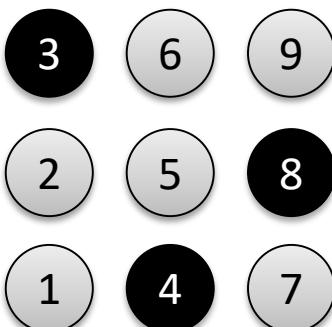
The Master Equation

Probability of configuration σ

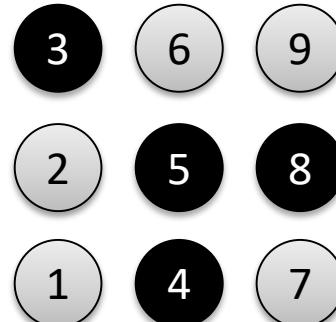
$$\frac{dP(\sigma)}{dt} = \sum_{\sigma'} \left[W_{\sigma' \rightarrow \sigma} \cdot P(\sigma') - W_{\sigma \rightarrow \sigma'} \cdot P(\sigma) \right]$$

Probability efflux to other configurations σ'

Probability influx from other configurations σ'



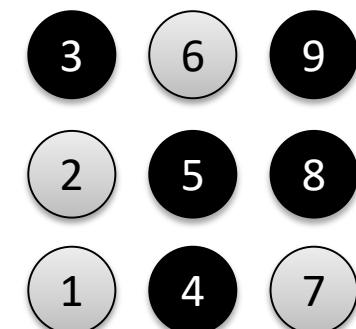
Adsorption on site 5



$$\sigma' = (0, 0, 1, 1, \textcolor{red}{0}, 0, 0, 1, 0)$$

$$\sigma = (0, 0, 1, 1, 1, 0, 0, 1, 0)$$

Adsorption on site 9



$$\sigma' = (0, 0, 1, 1, 1, 0, 0, 1, \textcolor{red}{1})$$

The Master Equation

Probability of configuration σ

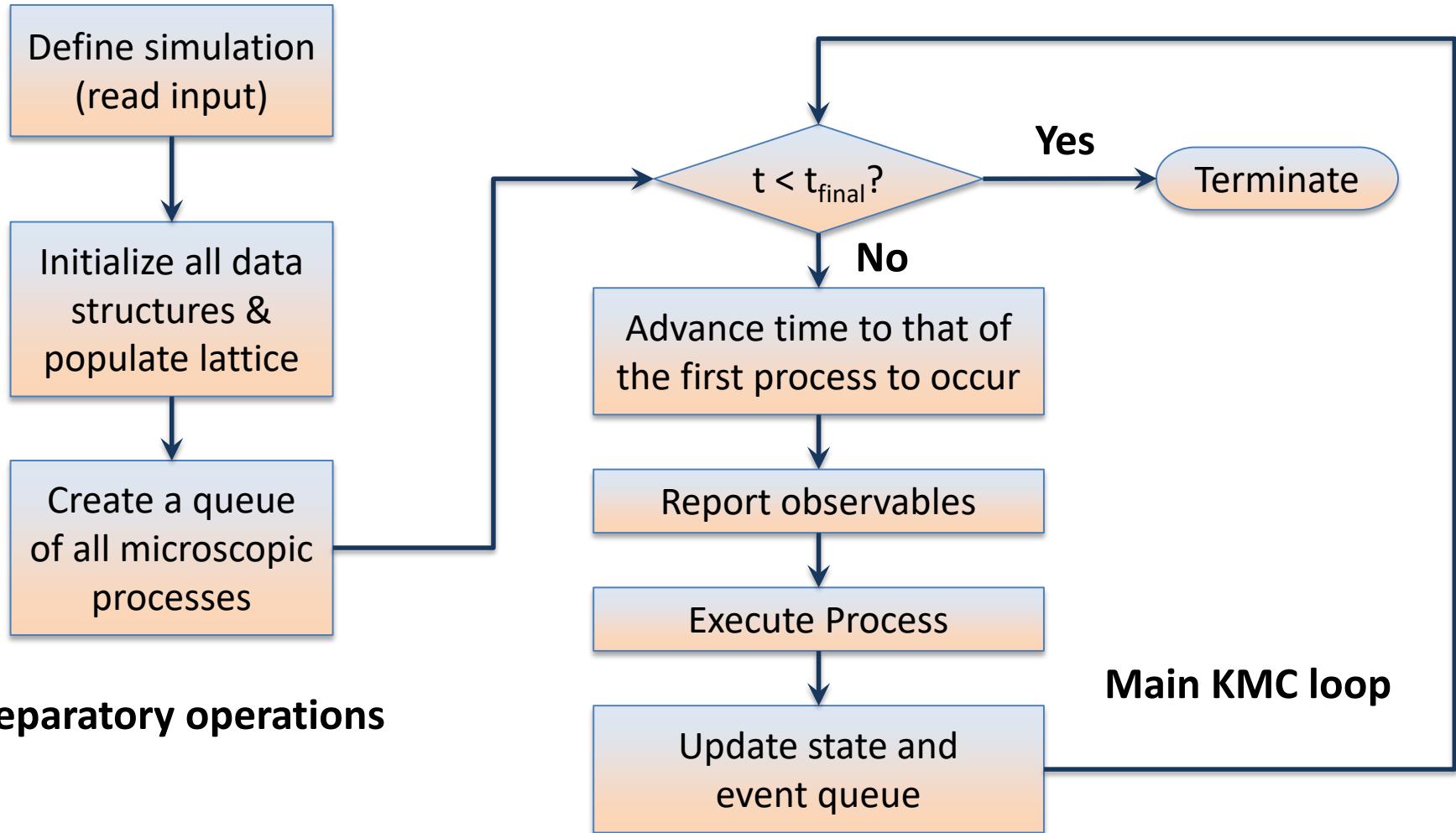
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Probability efflux to other configurations σ'

Probability influx from other configurations σ'

- Equation linear with respect to $P(\sigma)$ but **state space** often too large,
e.g. for lattice gas $2^{N_{\text{sites}}} = 5.62 \times 10^{14}$ for $N_{\text{sites}} = 49$
- ✓ We simulate & sample stochastic trajectories (KMC method)

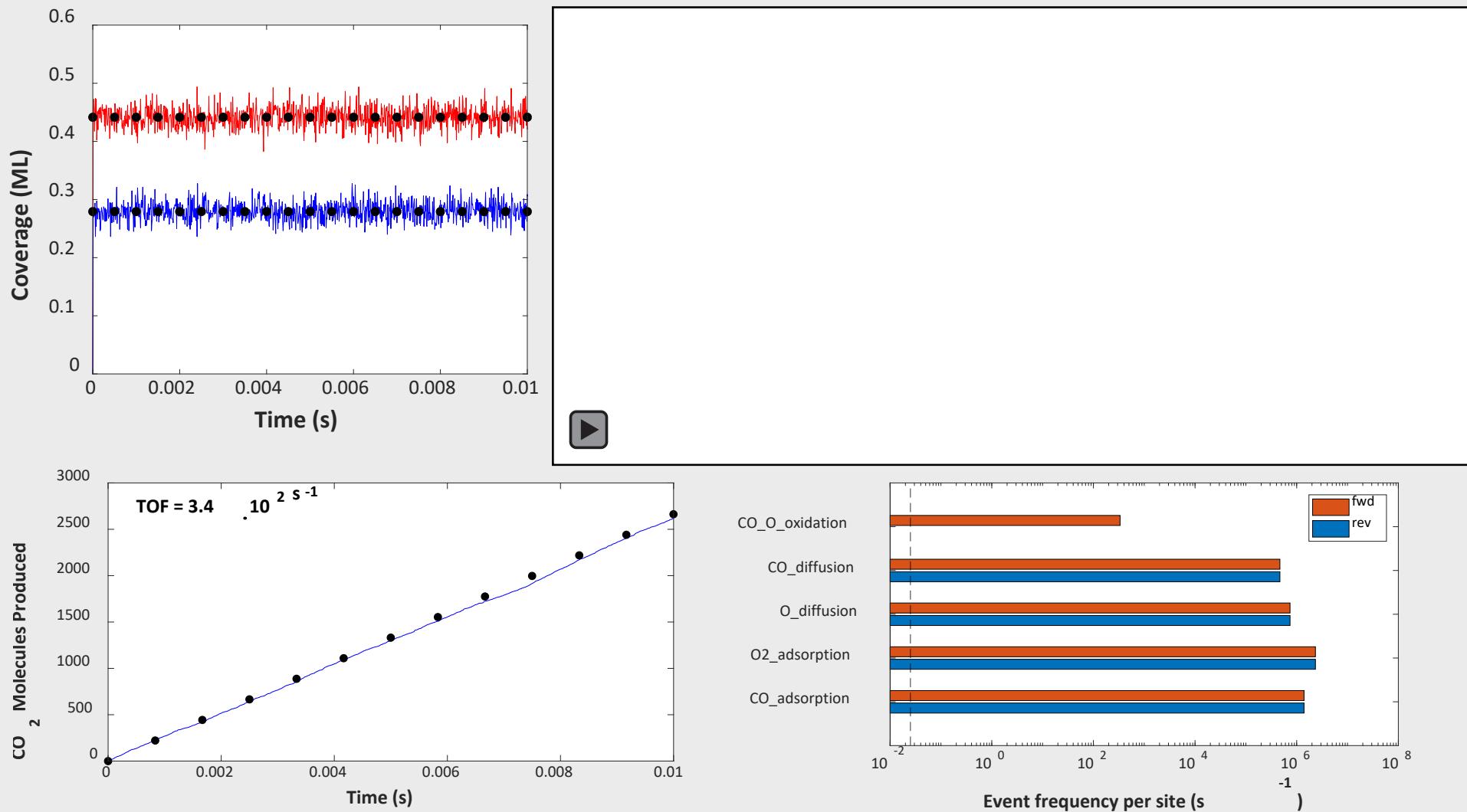
KMC Algorithm Flowchart



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.

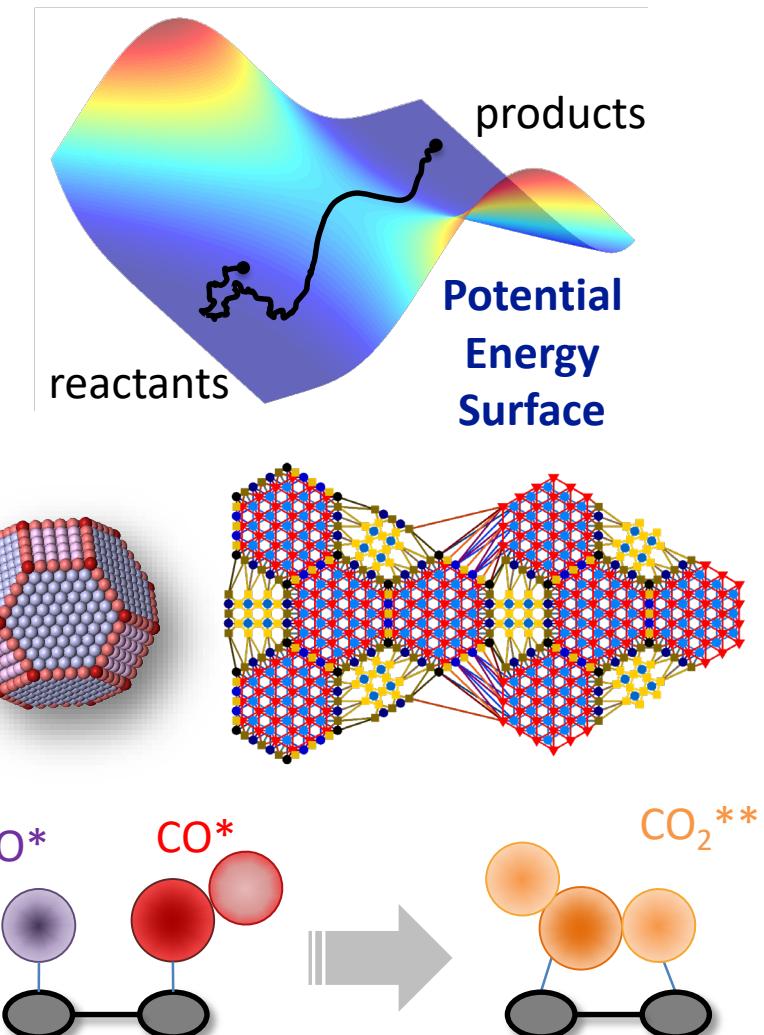
Typical KMC Output



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.

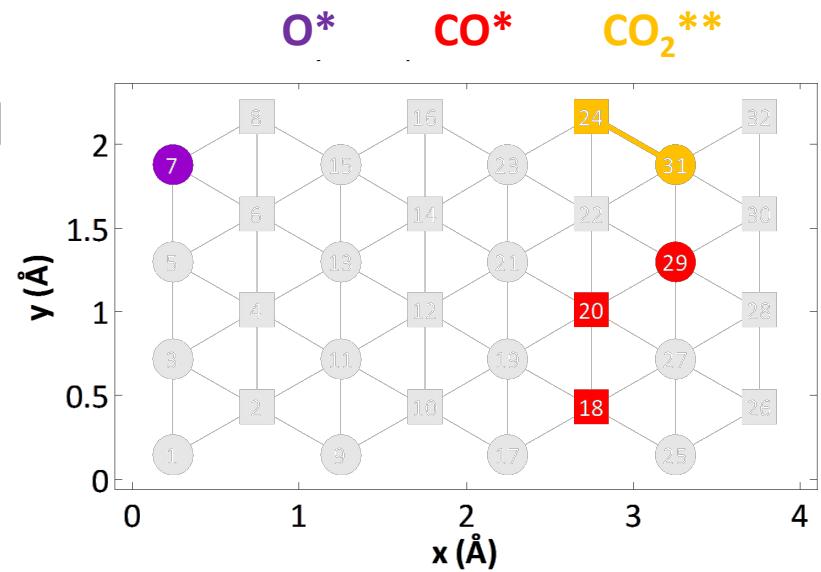
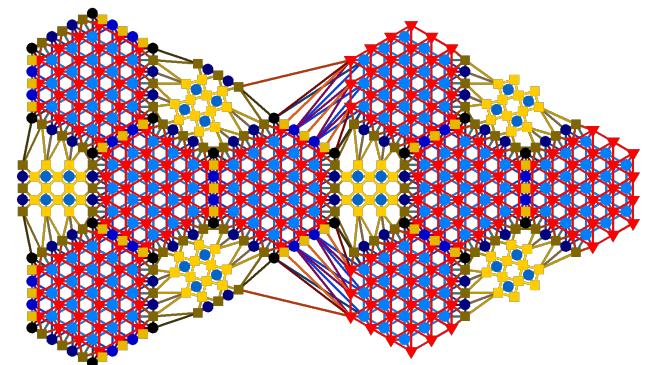
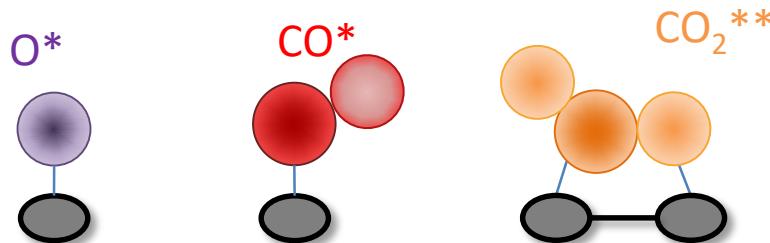
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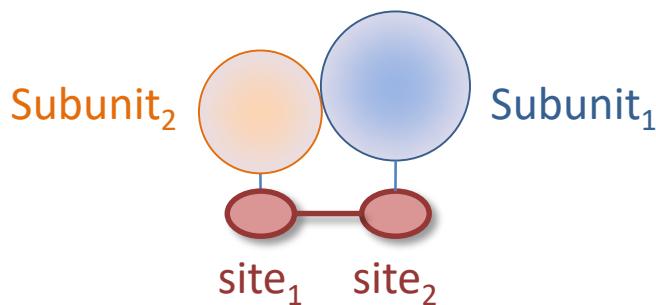


Graph-Theoretical KMC Approach

- 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

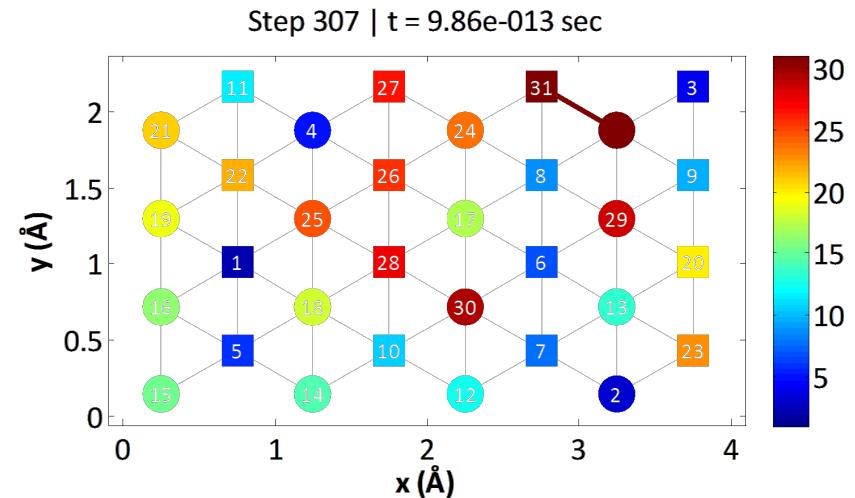
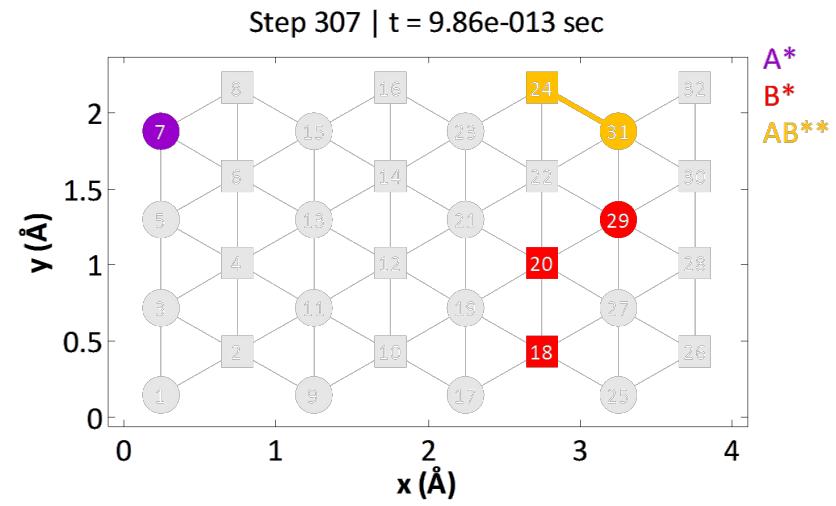


Lattice State Representation

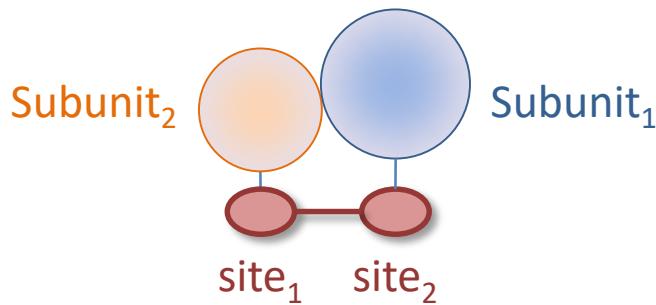


- **Multi-dentate** species modeled
(bind to more than one sites)
- Lattice represented as **graph**
- State species species & dentation \forall site

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

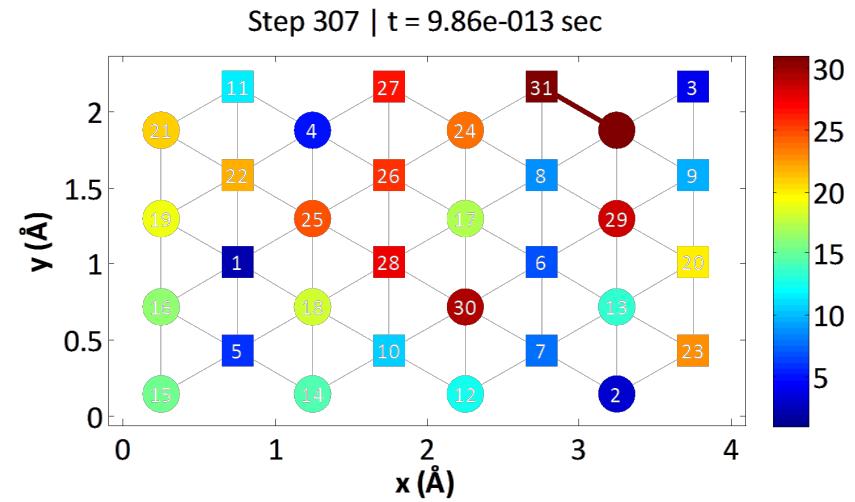
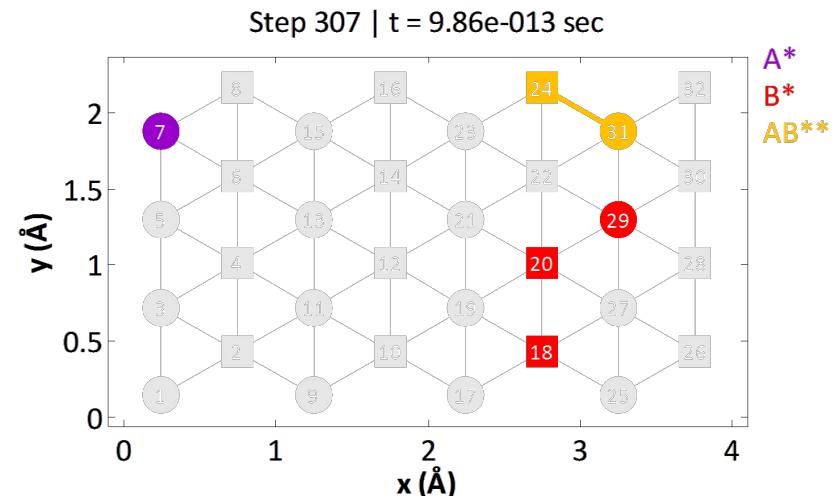


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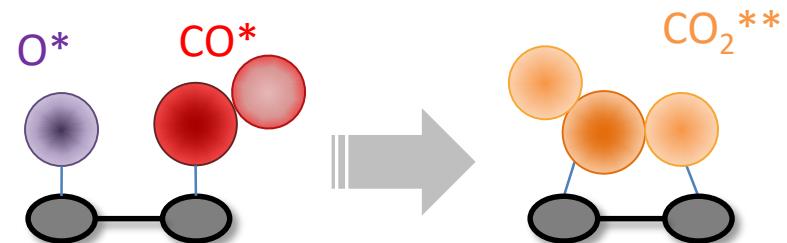
- Multi-dentate species modeled (bind to more than one sites)
- Lattice represented as **graph**
- State species species & dentation \forall site

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

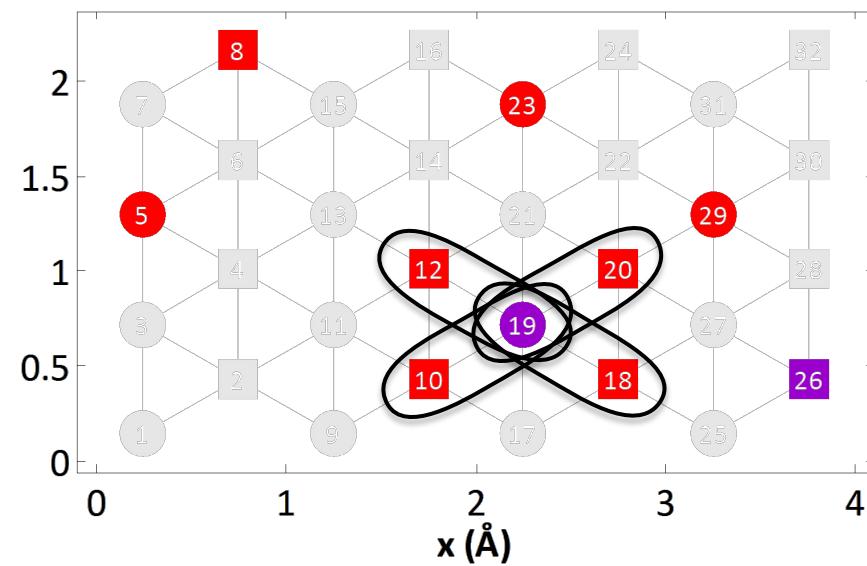


Elementary Step Representation

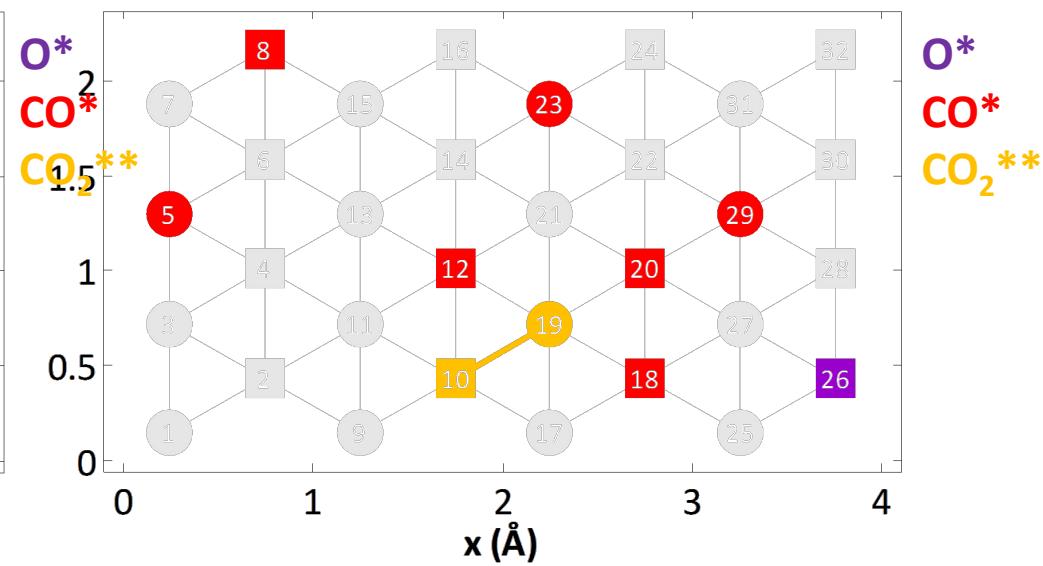
- Elementary steps → connected graphs
- Subgraph isomorphism used to
 - identify possible elementary steps
 - map them to lattice processes



Step 178 | $t = 5.83e-013$ sec



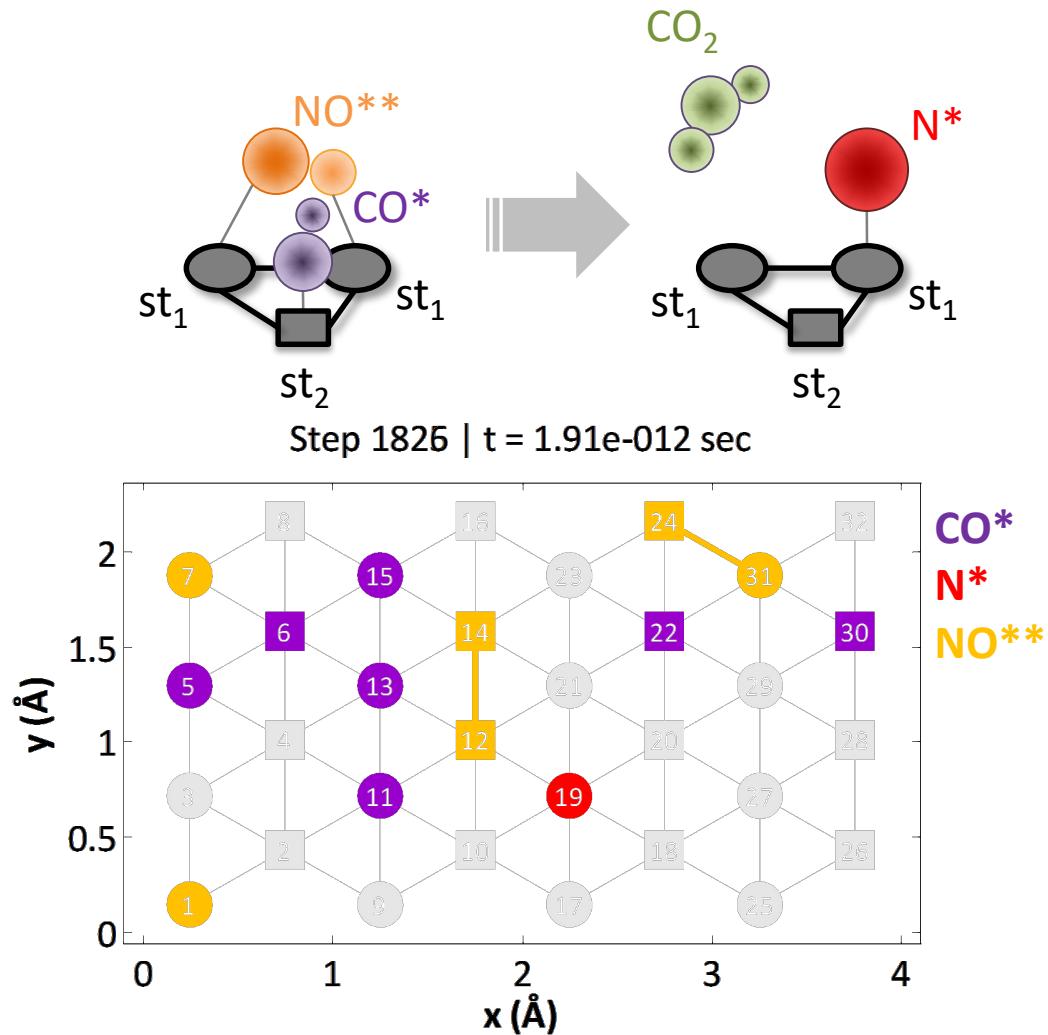
Step 179 | $t = 5.83e-013$ sec



Solving the Subgraph Isomorphism

- **Subgraph 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



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 \leftrightarrow 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?

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
:	:	:

Lattice
processes

Entity	#Procs	Processes
1	5	34, 12, 65, 74, 10
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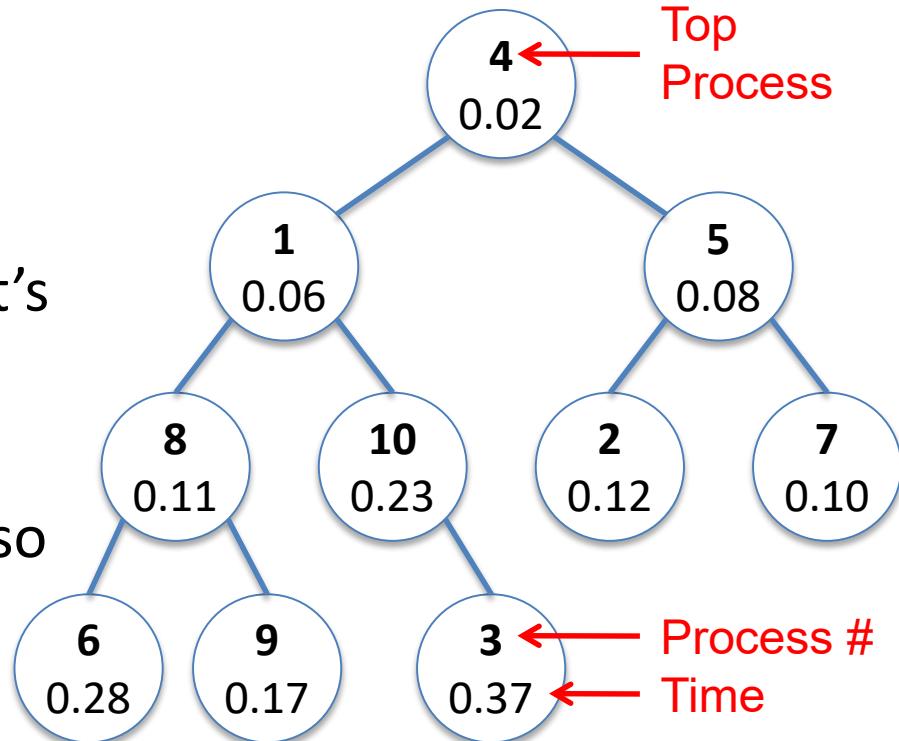
Lattice sites
Entities
(adsorbates or empty sites)

Site	Entity	Species	Dentate
1	15	0	1
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18	7	2	1
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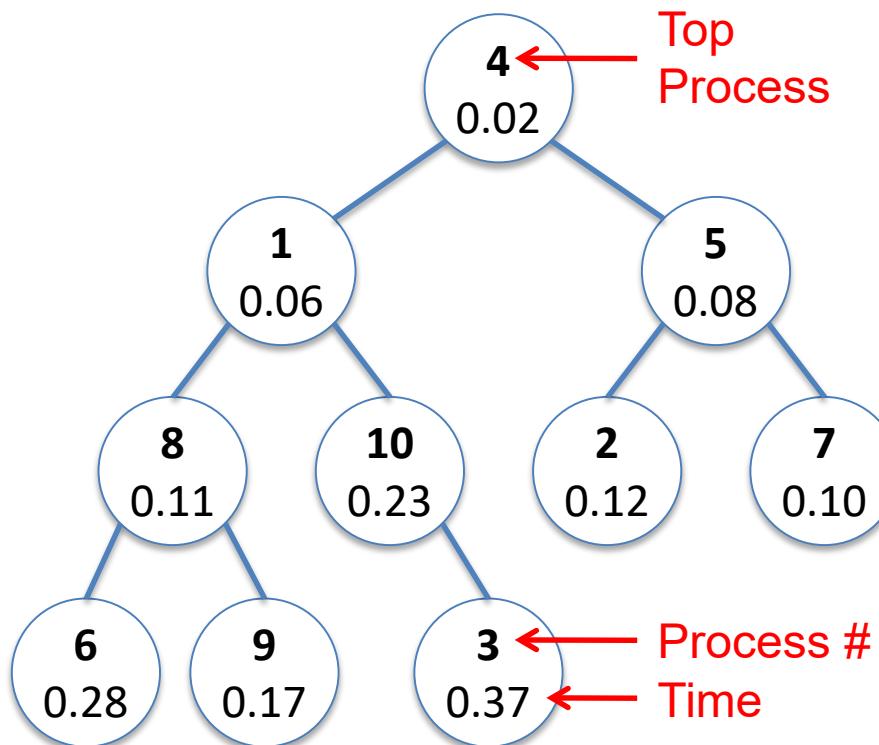
Selecting the Next Event to Happen

- 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



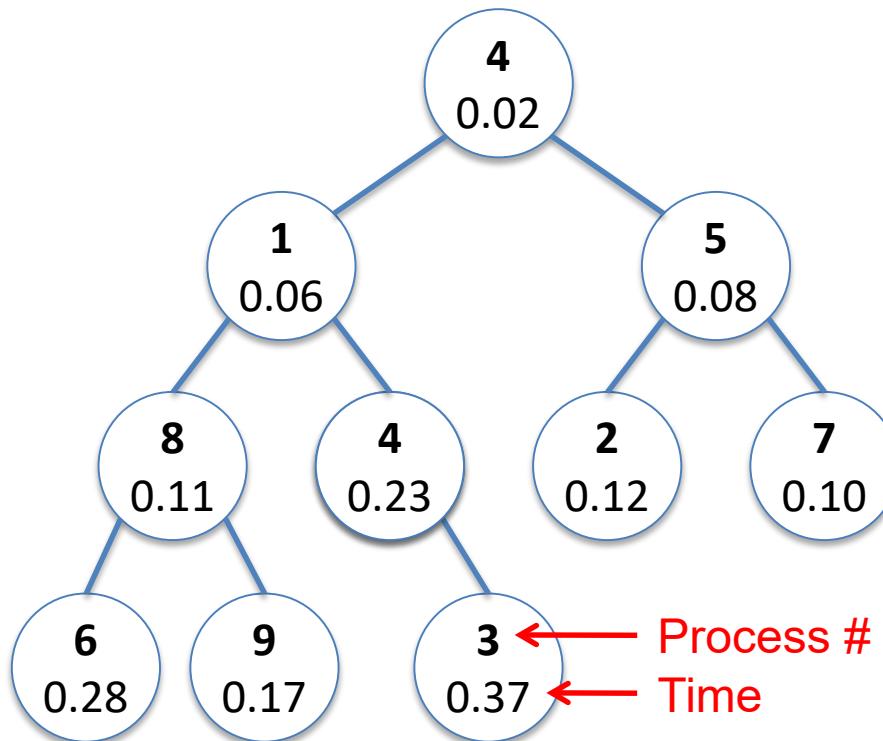
Use of Heap Arrays for Queue Construction

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



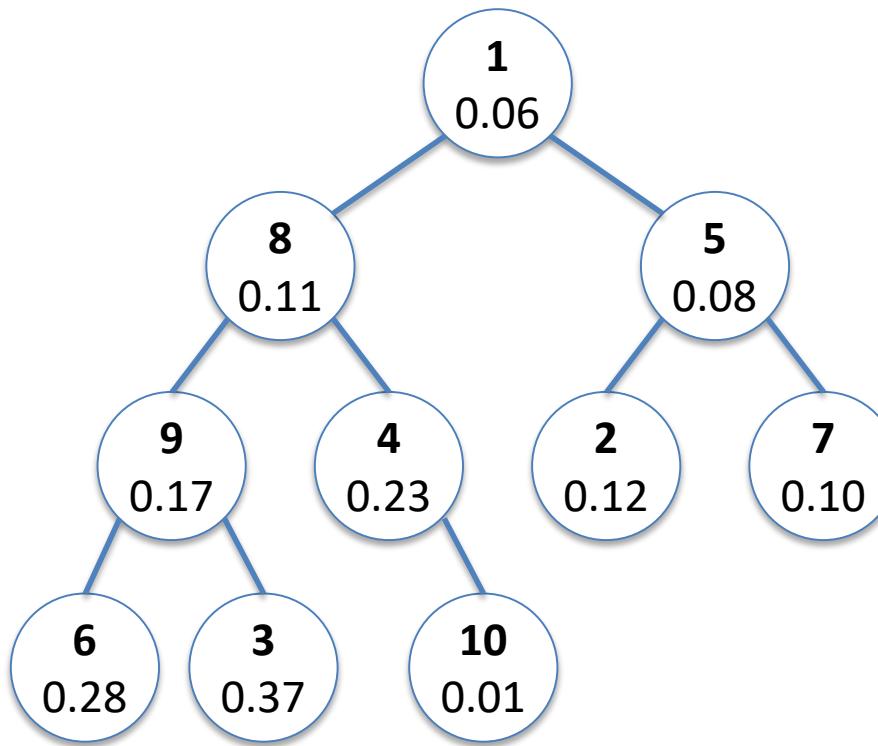
Heap Removal Operation

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



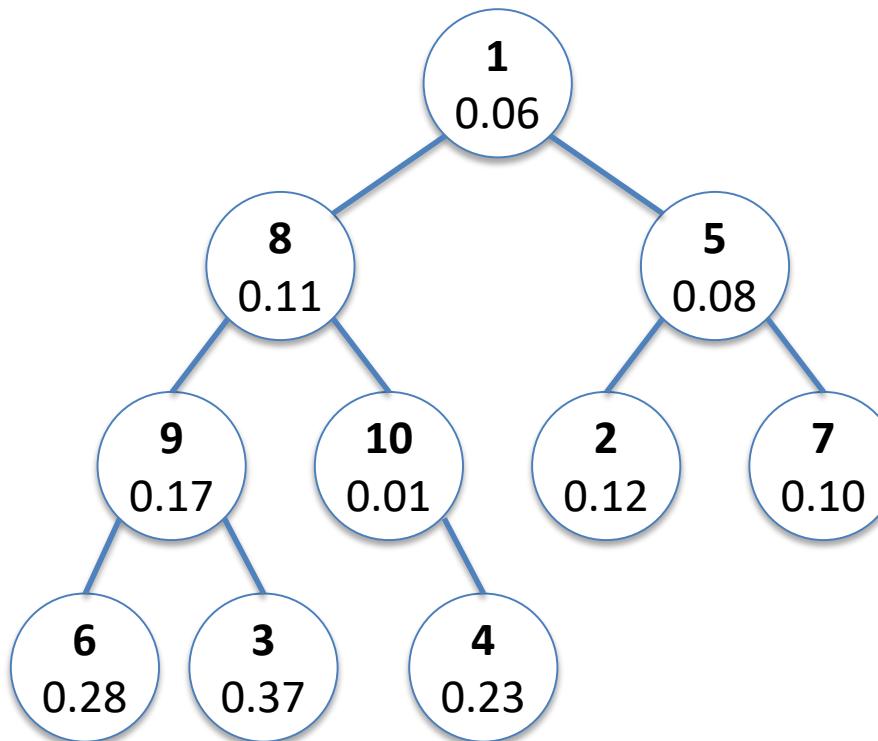
Heap Addition Operation

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



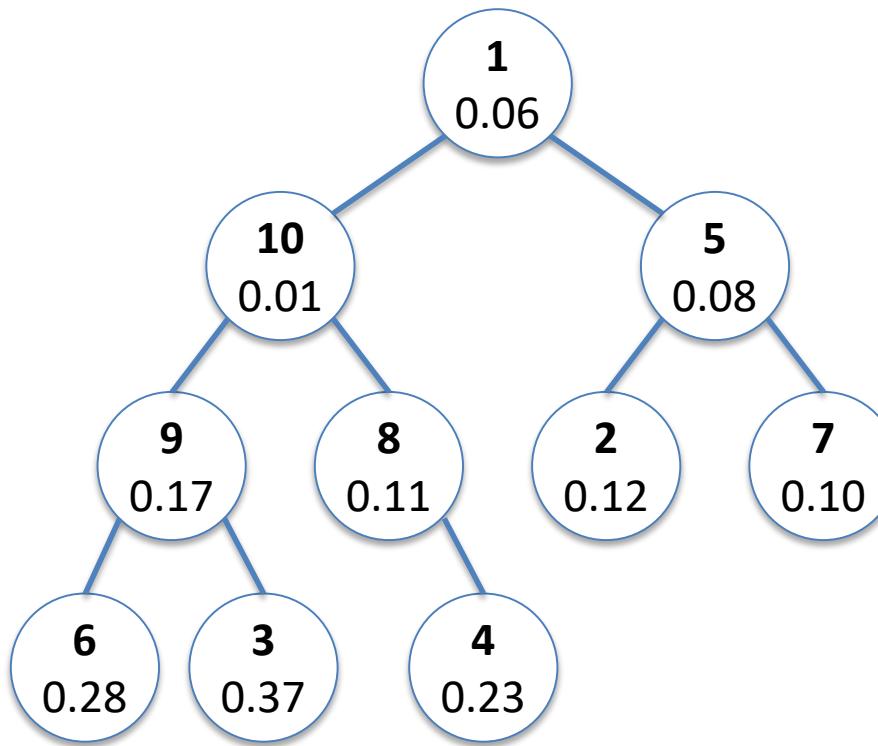
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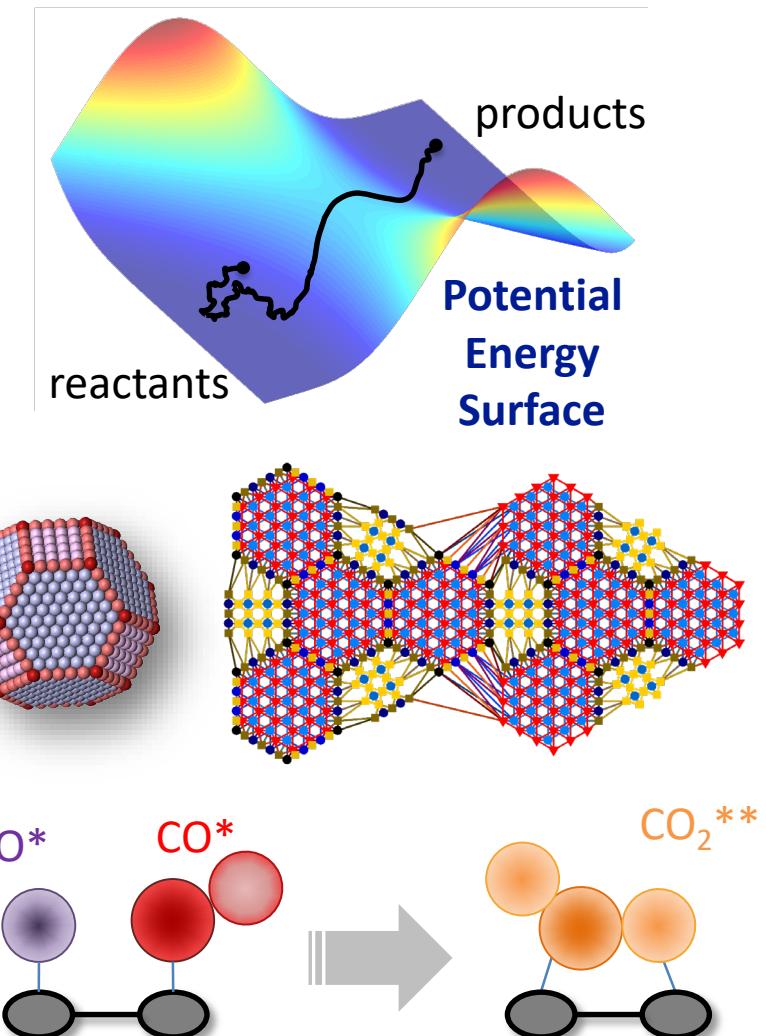


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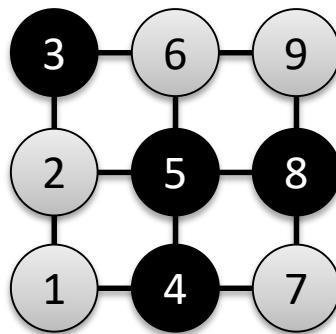
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Non-ideal Adlayers

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



$$E_{\text{tot}} = 4 \cdot E(\text{Single body terms}) + 2 \cdot E(\text{Interaction energies}) + \dots$$

Single body terms
 (adsorption energies)

Interaction energies
 (2-body and many-body)

- In the general case: cluster expansion

$$\mathcal{H}(\sigma) = \sum_{k=1}^{N_c} \frac{\text{ECI}_k}{\text{GM}_k} \cdot \text{NCE}_k(\sigma)$$

Effective cluster interaction
 Number of instances
 of interactions pattern
 Graph multiplicity

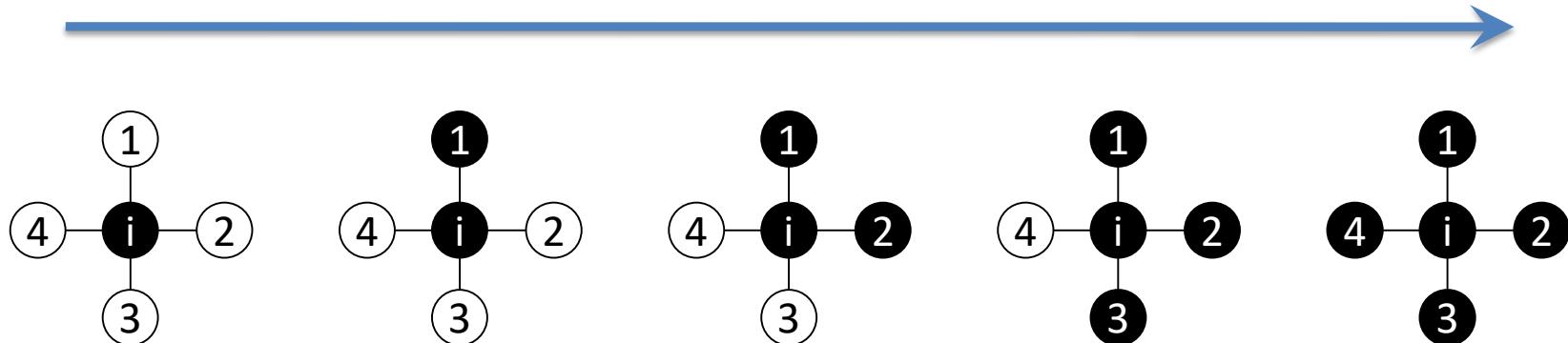
Patterns represented as graphs, detected using same ideas as for reactions...

Modelling Coverage Effects

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

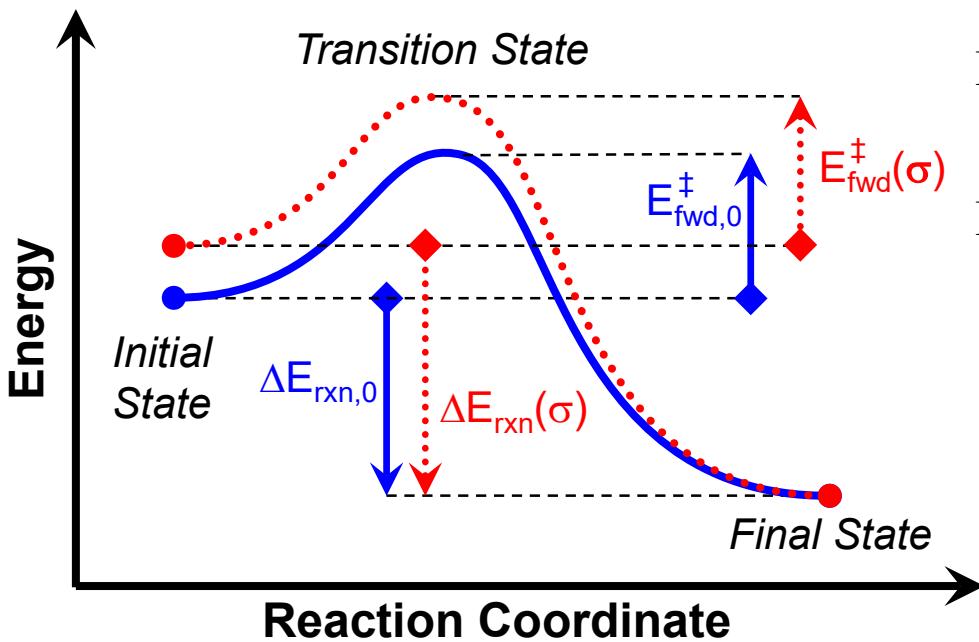
$$W_{\text{des},i} = A_{\text{des}} \cdot \exp \left(-\frac{E_a - J_{\text{int}} \cdot \sum_{j \in \mathcal{N}_i} \sigma_j}{k_B \cdot T} \right) \cdot \sigma_i$$

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



Treating the general case?

Brønsted-Evans-Polanyi Relations



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

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

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

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

... as expected (micro-reversibility)

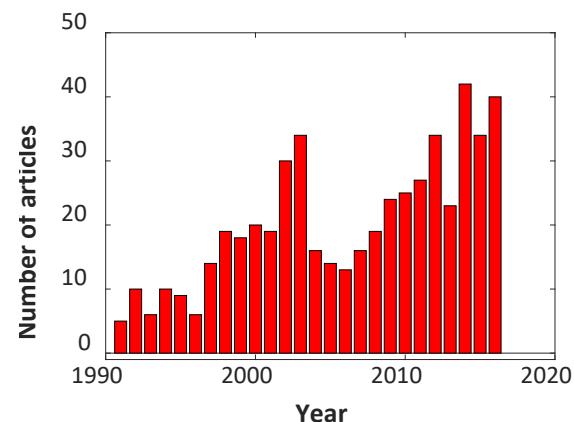
- Linear correlation between activation and reaction energy
- Captures effect of local reaction environment on rate

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



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