# Kinetic Monte Carlo modelling with “kmos”

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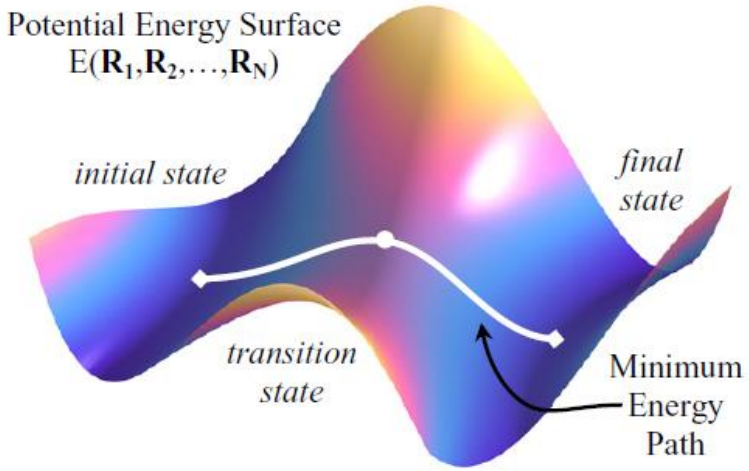
# Simulation techniques for chemical kinetics

| | Molecular dynamics | (lattice) Kinetic Monte Carlo | Mean-field approximation |
|---|---|---|---|
| **Treatment of space** | Continuous 3D | Discrete (lattice) | None |
| **State variables** | Atomic positions and velocities | Occupancies of lattice sites | Species coverages |
| **Treatment of reactions** | Simulate all vibrations and barrier crossings | Markovian state-to-state dynamics | Rate equations |



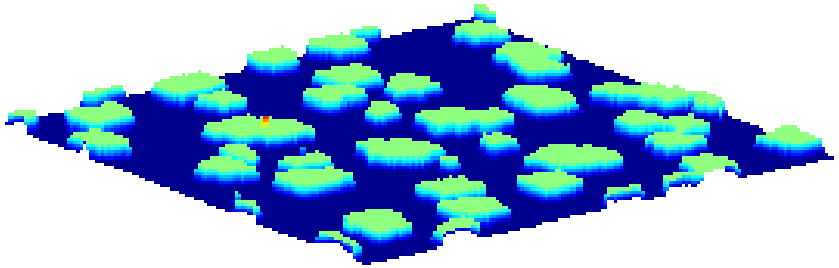

## Why kinetic Monte Carlo?

- Molecular dynamics limited to short timescales and few “interesting” events.
- Mean-field approximation neglects spatial inhomogeneity.

*M. Stamatakis, J. Phys. Condens. Matter **27**, 013001 (2015)*

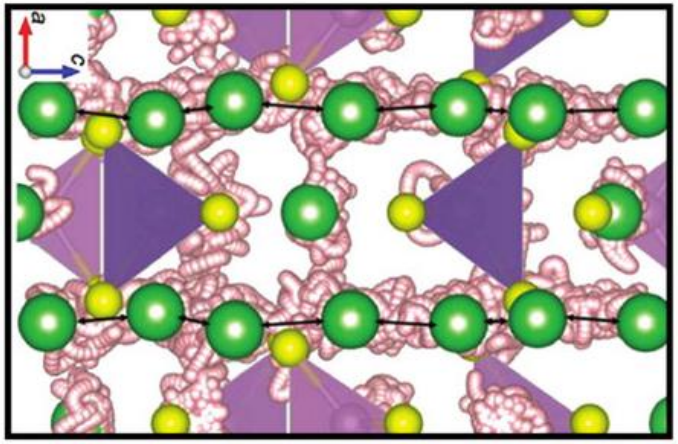
# Applications of kinetic Monte Carlo simulations

**Crystal growth**



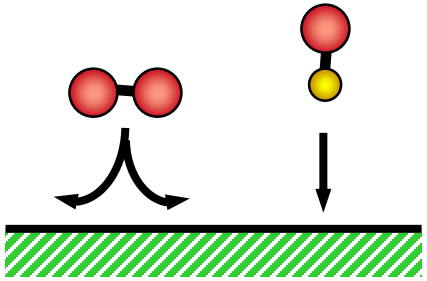
*http://www.lce.hut.fi/publications/annual2000/node22.html*

**Diffusion in battery materials**



*Urban et al., npj Computational Materials **2**, 16002 (2016)*

**Heterogeneous catalysis**



*Reuter, K., in Modelling and Simulation of Heterogeneous Catalytic Reactions: From the Molecular Process to the Technical System, O. Deutschmann, Editor. 2011, Wiley-VCH: Weinheim. p. 71-112*

# Practical approach

Determine all possible processes in a given system configuration (lattice occupation):

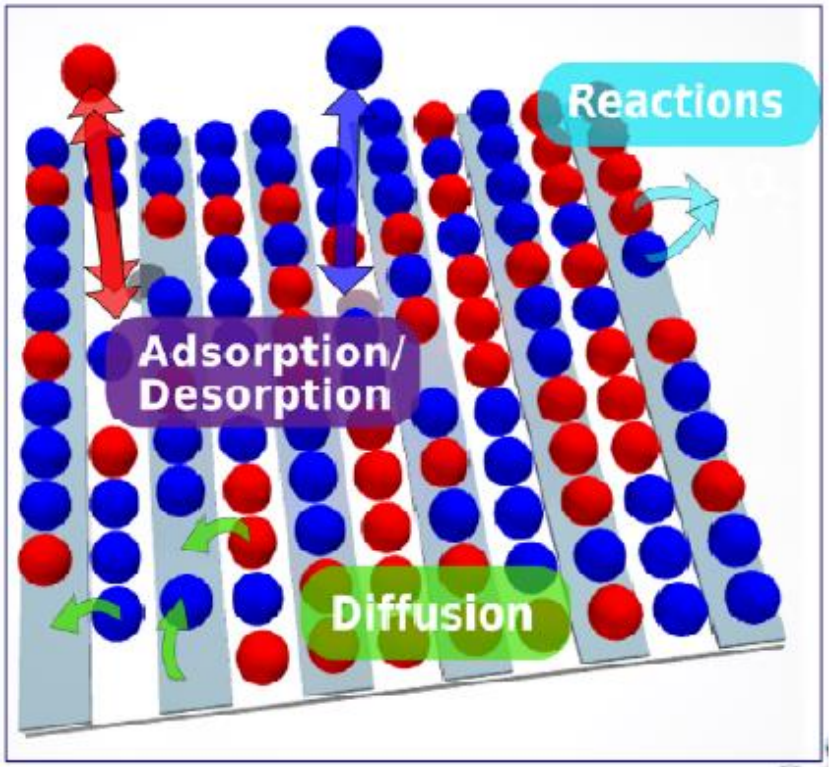
- Adsorption
- Desorption
- Diffusion
- Reaction

Kinetic parameters needed as input:

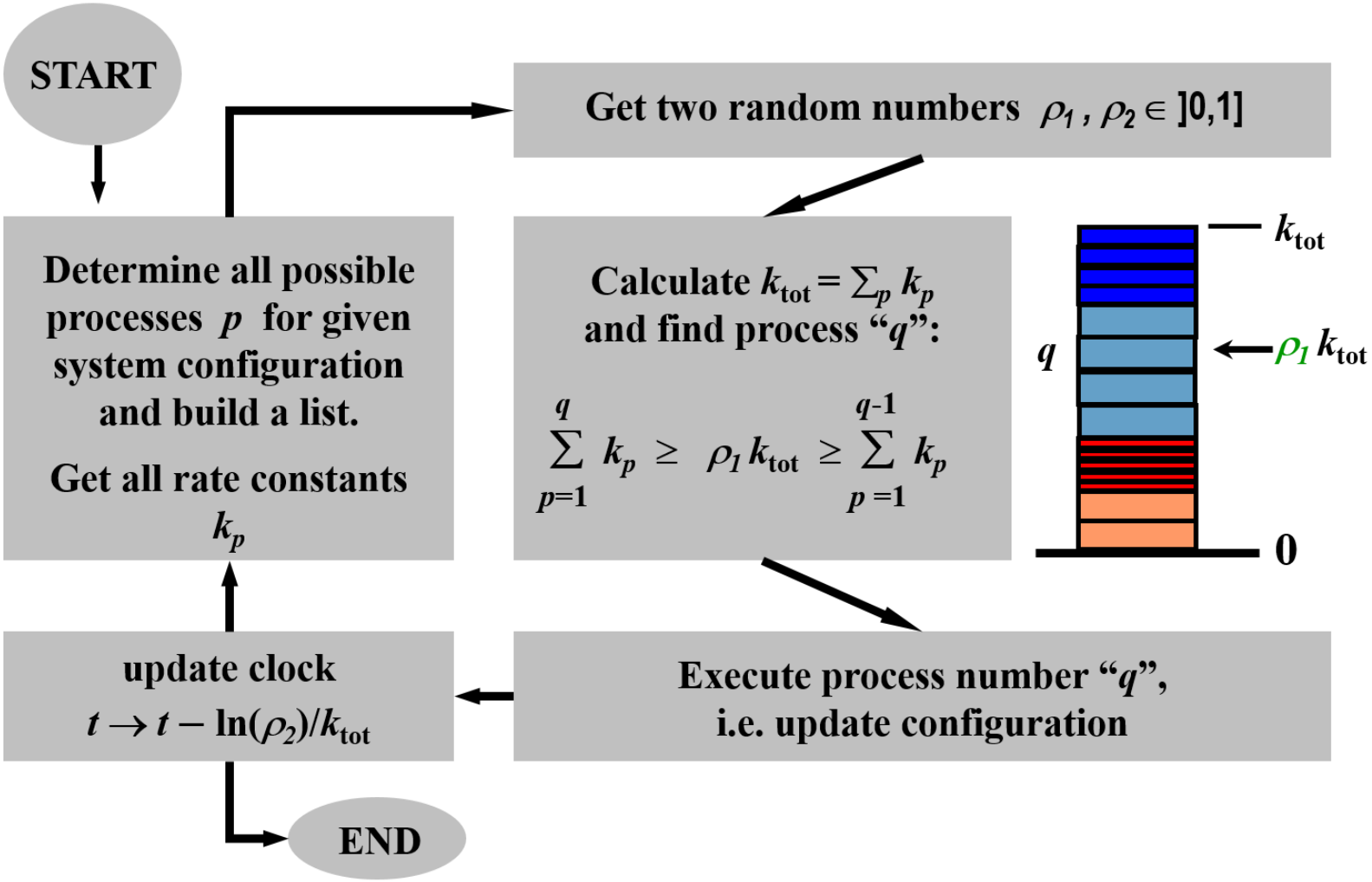
- Experimental data
- First-principles calculations

Achieve numerical solution to Master equation:

$$\frac{dP_i(t)}{dt} = -\sum_j k_{i\to j} P_i(t) + \sum_j k_{j\to i} P_j(t)$$

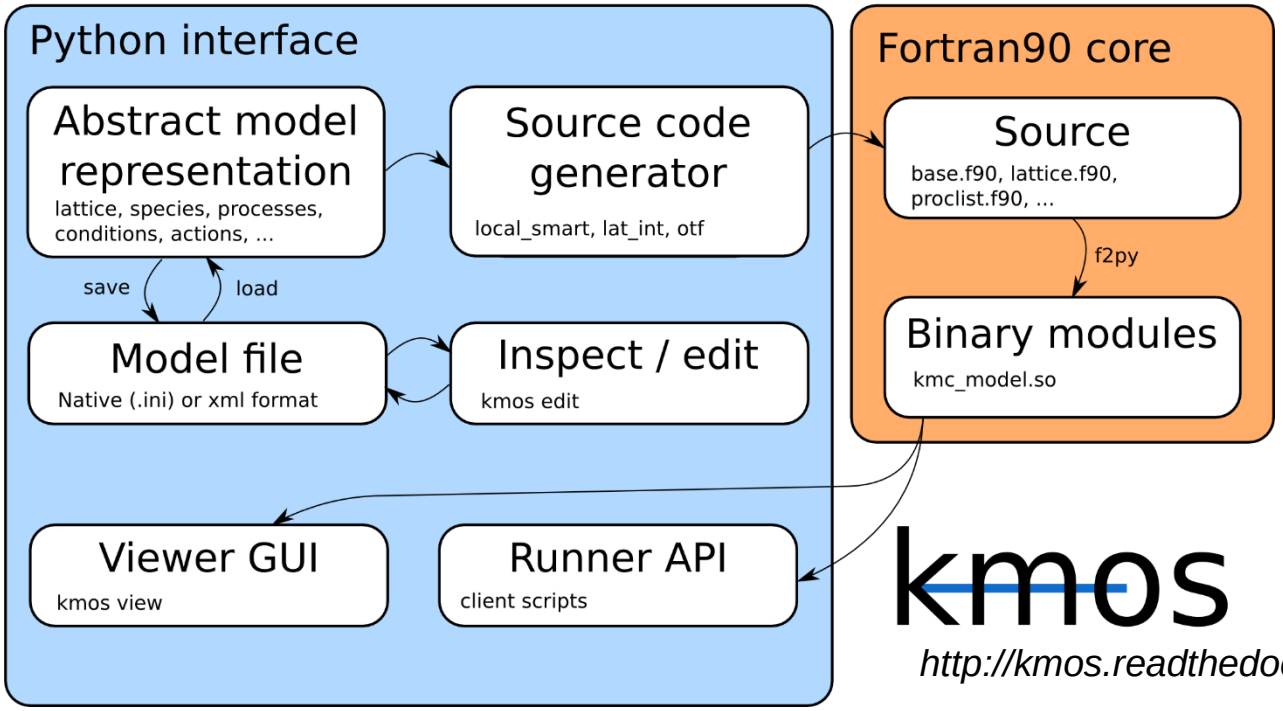


# Variable step-size method (VSSM)



# The “kmos” framework

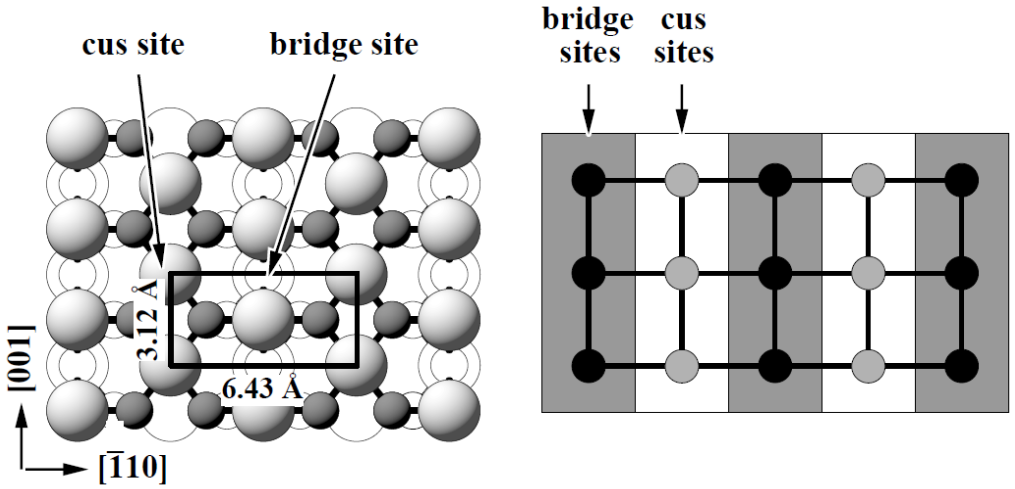
- Highly efficient Fortran90 code generated from abstract model definition in Python.
- Allows for efficient local updates of enabled and disabled events (required for VSSM).
- Storage and exchange of kMC models through XML data format.
- Python interface (f2py) to run and evaluate the model.
- Graphical user interface (GUI) and application programming interface (API).




kmos

*http://kmos.readthedocs.io/en/latest/*

# Example: CO oxidation @ $RuO_2(110)$



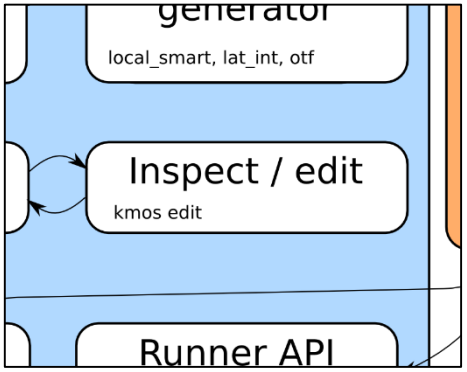

Surface structure

DFT input data

| | $E_b$ | $\Delta E^{\mathrm{des}}$ | | | $\Delta E^{\mathrm{diff}}$ | |
|---|---|---|---|---|---|---|
| | | unimol. | with $O^{br}$ | with $O^{cus}$ | to br | to cus |
| $CO^{br}$ | -1.6 | 1.6 | 1.5 | 0.8 | 0.6 | 1.6 |
| $CO^{cus}$ | -1.3 | 1.3 | 1.2 | 0.9 | 1.3 | 1.7 |
| $O^{br}$ | -2.3 | – | 4.6 | 3.3 | 0.7 | 2.3 |
| $O^{cus}$ | -1.0 | – | 3.3 | 2.0 | 1.0 | 1.6 |

*Reuter, K., in Modelling and Simulation of Heterogeneous Catalytic Reactions: From the Molecular Process to the Technical System, O. Deutschmann, Editor. 2011, Wiley-VCH: Weinheim. p. 71-112*

# Getting first impressions: Using the Editor GUI




In folder containing xml file type:

`kmos edit model.xml`