

First-principles Multi-scale Simulations of Dynamic Catalyst Surfaces / CO Oxidation from Palladium Surface Oxide to Palladium Metal

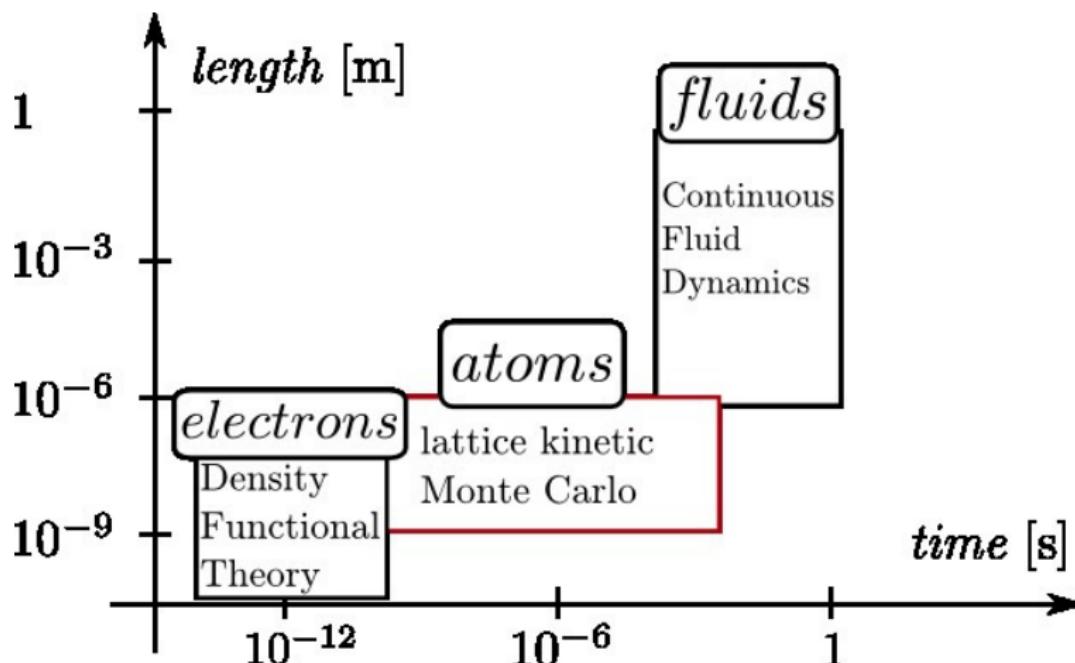
Max J. Hoffmann

Chair of Theoretical Chemistry & Catalysis Research Center
TU München, Germany

July 24, 2014

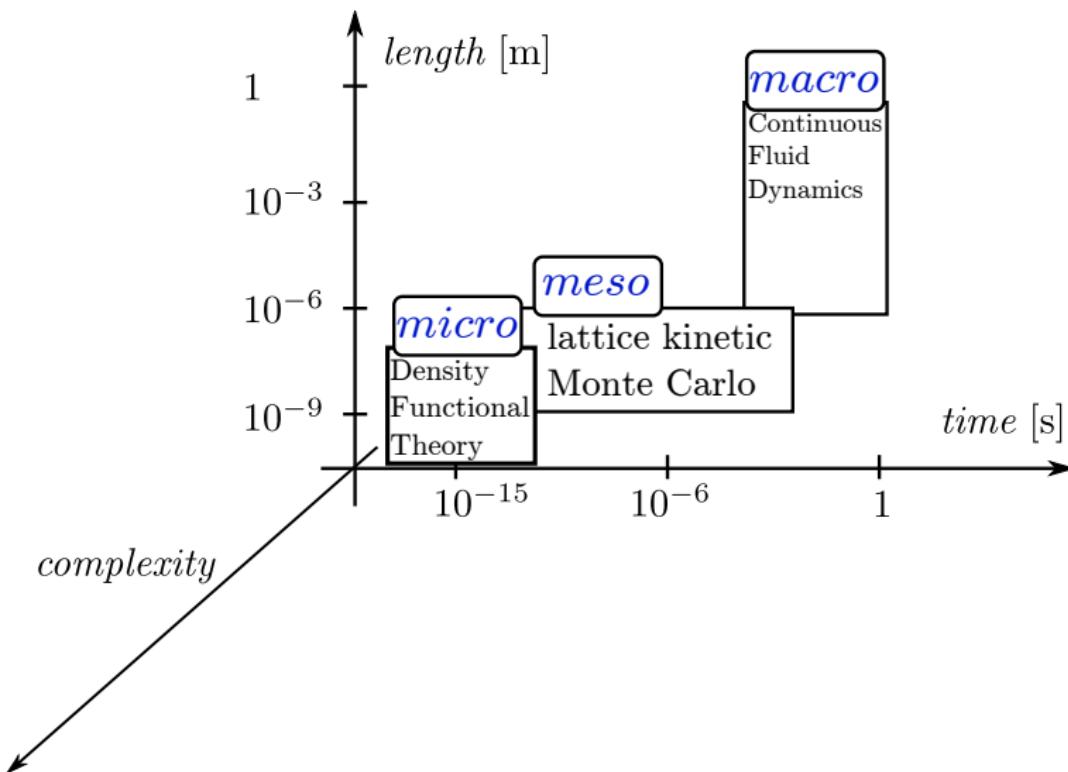
Heterogeneous Catalysis

First-principles multi-scale modeling and complexity



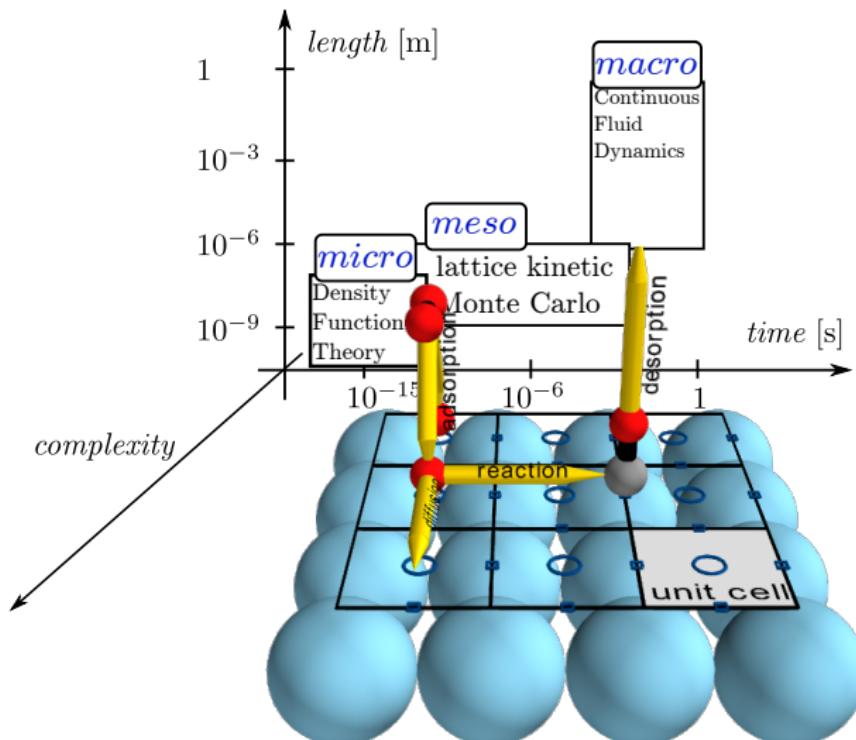
Heterogeneous Catalysis

First-principles multi-scale modeling and complexity



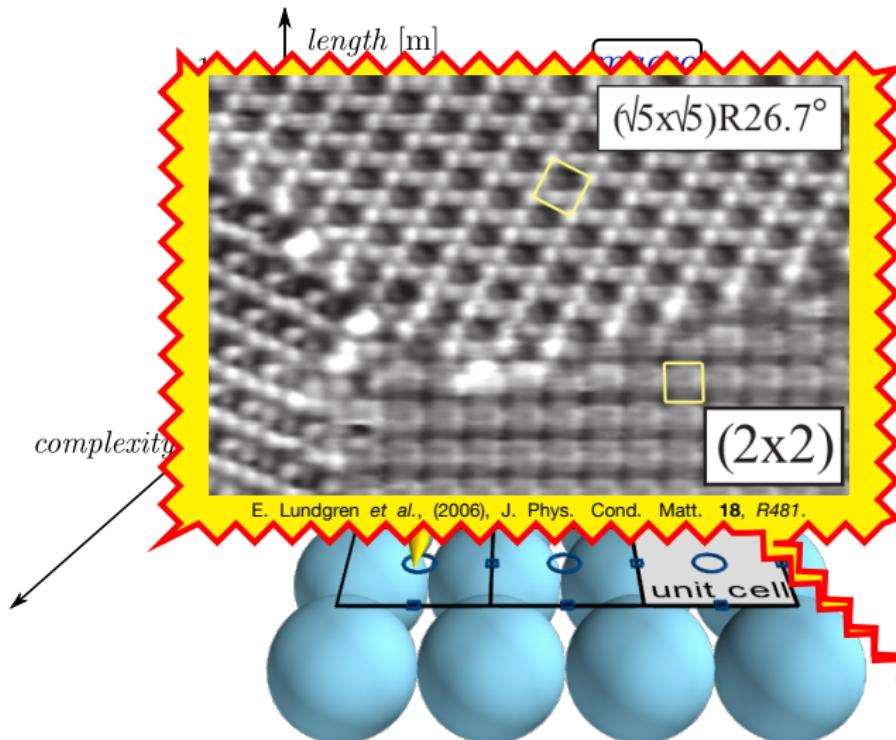
Heterogeneous Catalysis

First-principles multi-scale modeling and complexity

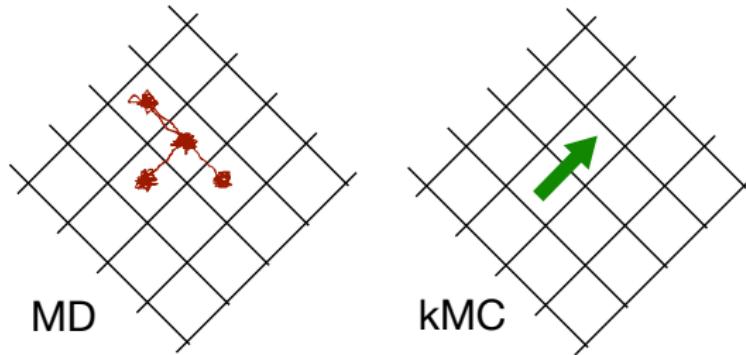


Heterogeneous Catalysis

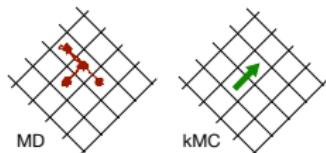
First-principles multi-scale modeling and complexity



First-principles kinetic Monte Carlo



First-principles kinetic Monte Carlo



Follow rare-event time evolution by numerically solving Markovian master equation:

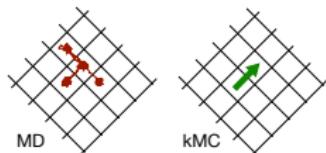
$$\dot{\rho}_i = \sum_j (-k_{ji}\rho_i + k_{ij}\rho_j)$$

Using harmonic transition state theory

$$k_{ij} = f^{\text{TST}} \frac{k_{\text{B}} T}{h} \exp \left(\frac{-\Delta E_{ij}}{k_{\text{B}} T} \right)$$

K Reuter and M Scheffler, PRB **73**, 4, 045433 (2006).

First-principles kinetic Monte Carlo



Follow rare-event time evolution by numerically solving Markovian master equation:

$$\dot{\rho}_i = \sum_j (-k_{ji}\rho_i + k_{ij}\rho_j)$$

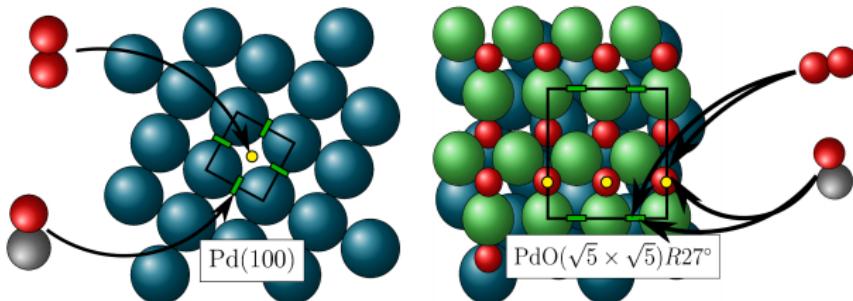
Using harmonic transition state theory

$$k_{ij} = f^{\text{TST}} \frac{k_B T}{h} \exp\left(\frac{-\Delta E_{ij}}{k_B T}\right)$$

DFT(vibrations, barriers)
CASTEP GGA-PBE
 $E_{\text{cut}} = 400$ eV, U.S.-PP,
2-4 layer slabs

K Reuter and M Scheffler, PRB **73**, 4, 045433 (2006).

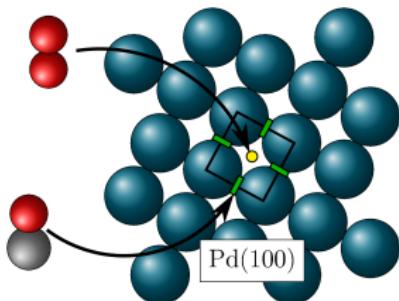
Kinetic Bistability



MJH and K Reuter, Top. Catal. 57, 159 (2014)

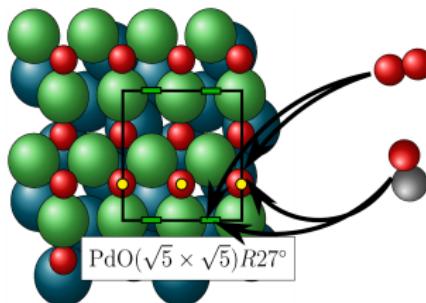
metal vs. oxide

Kinetic Bistability



Pd(100)

- lateral interactions through n.n. site blocking

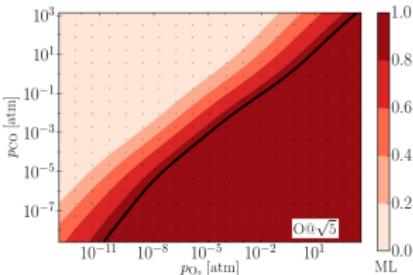
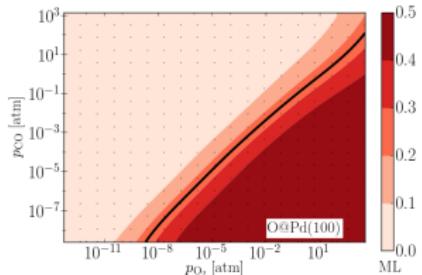
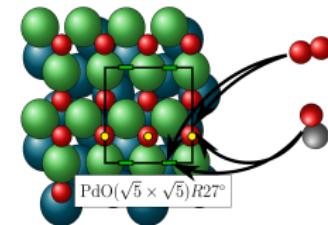
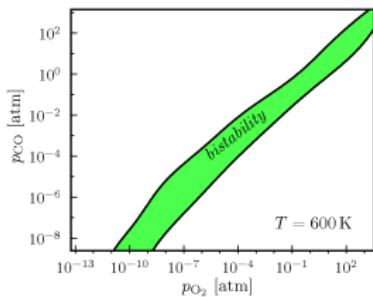
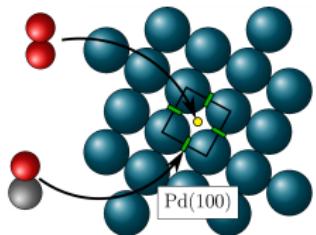


PdO $(\sqrt{5} \times \sqrt{5}) R27^\circ$

- no lateral interactions, DFT binding energies for intact surface oxide
- Eley-Rideal reaction

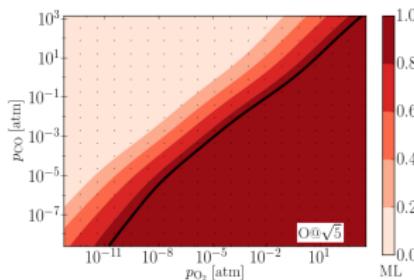
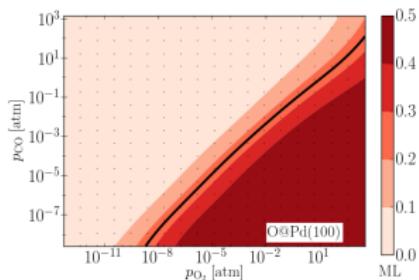
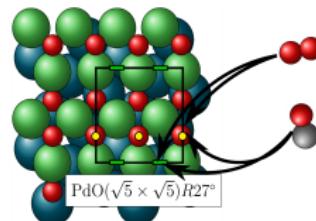
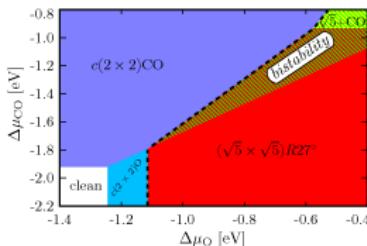
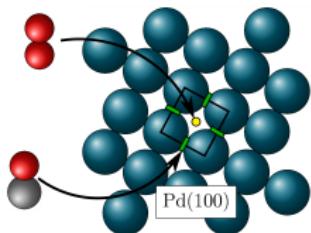
MJH and K Reuter, Top. Catal. 57, 159 (2014)

Kinetic Bistability



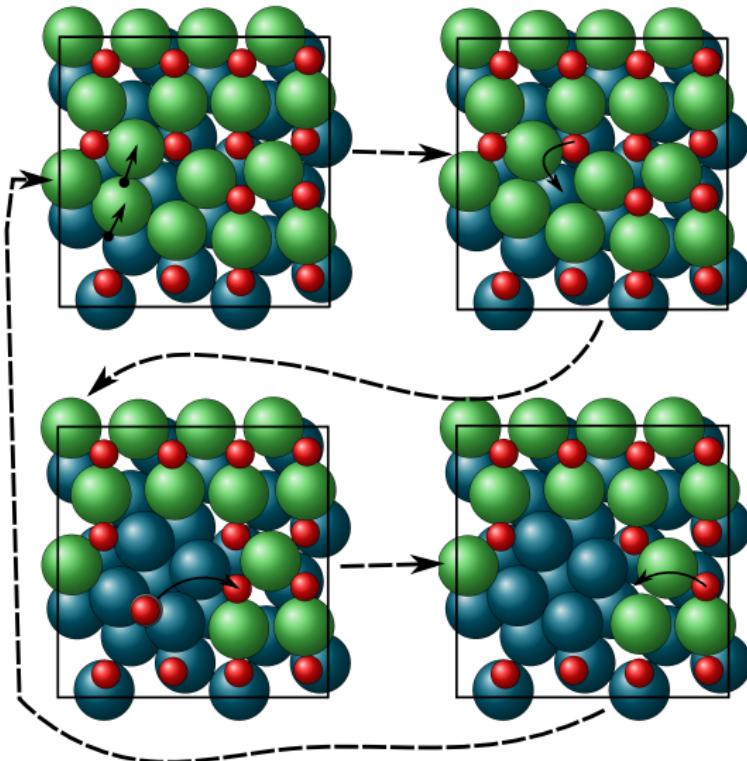
MJH and K Reuter, Top. Catal. 57, 159 (2014)

Kinetic Bistability



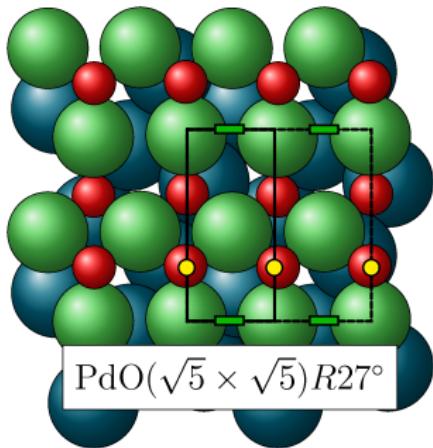
MJH and K Reuter, Top. Catal. 57, 159 (2014)

Multi-lattice reduction model

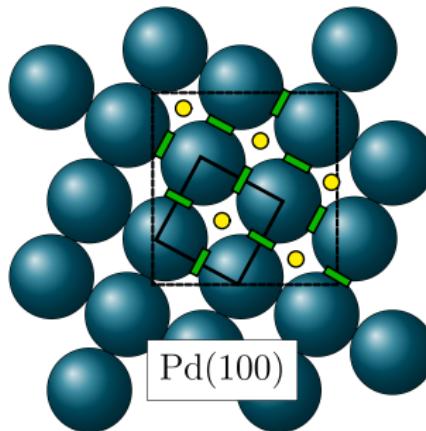


Multi-lattice kinetic Monte Carlo

1. Choose a unit cell commensurate to all lattices involved
2. Use a *null* species to model inactive sites

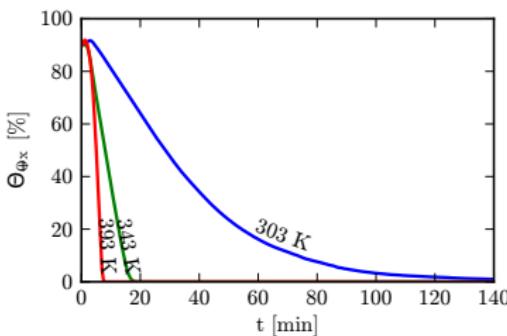
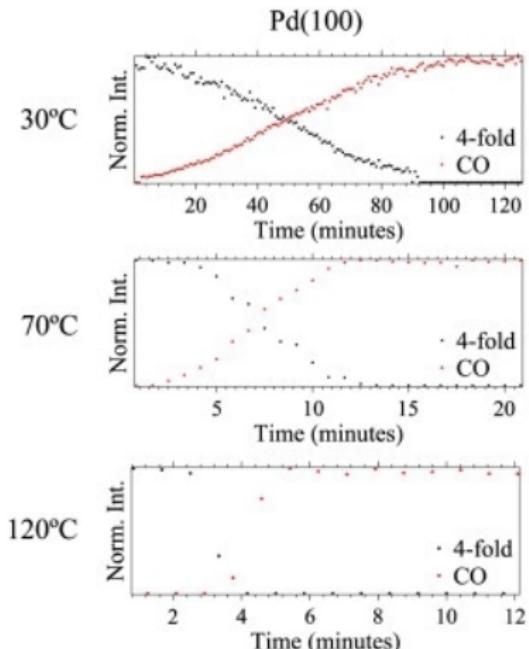


... × 2



... × 5

Multi-lattice reduction model

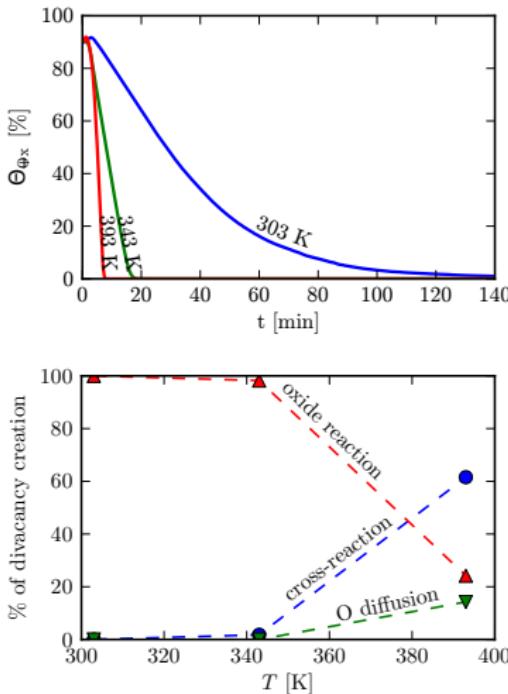
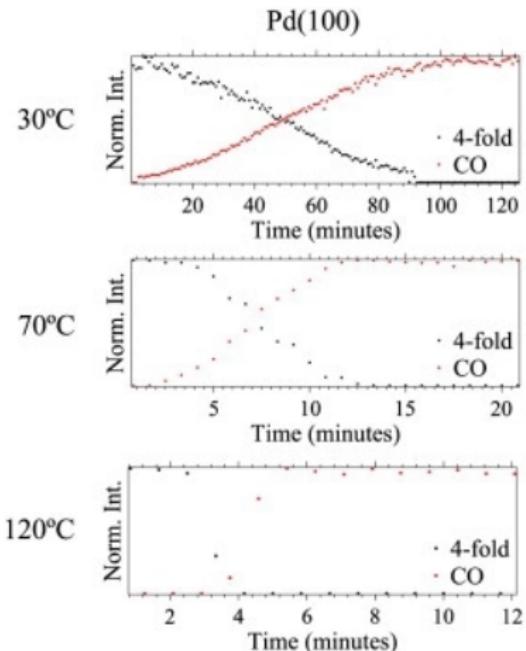


- 303 K, 343 K, 393 K
- $p_{CO} = 5 \times 10^{-11}$ bar
- No oxygen partial pressure

MJH, M Scheffler, K Reuter, (in preparation), 2014.

V. Fernandes *et al.*, Surf. Sci. **621**, 31-39 (2014).

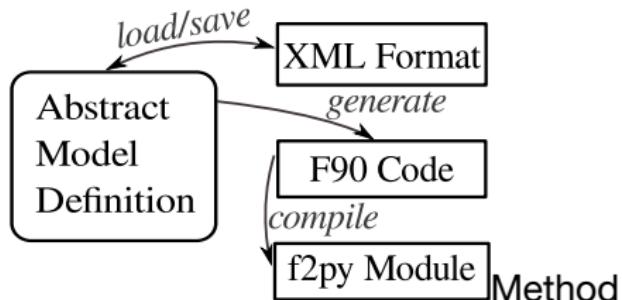
Multi-lattice reduction model



V. Fernandes *et al.*, Surf. Sci. **621**, 31-39 (2014).



A general lattice kMC framework



development:

MJH

Dr. Sebastian Matera

Felix Engelmann

Applications:

Maxime Van den Bossche,
Chalmers University

Dr. Sebastian Matera, Einstein
Center, Berlin

Byeongjin Baek, University of
Houston

Luke Roling, Iowa State University

Aditya Savara, ORNL

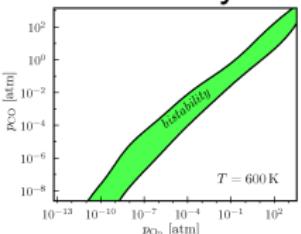
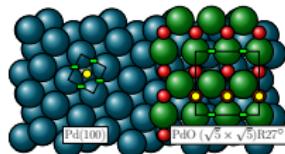
Tongyu Wang, Dr. Farnaz
Sotoodeh, Juan-Manuel Lorenzi

Andreas Garhammer, TUM



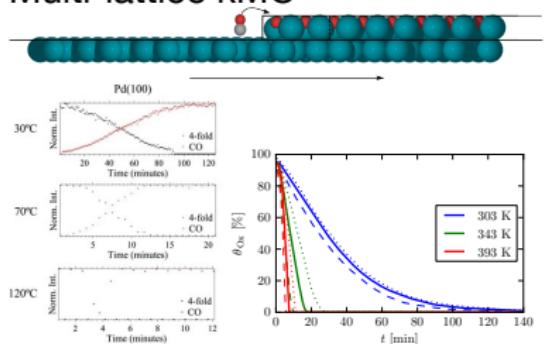
Summary

Metal/Surface Oxide Bistability



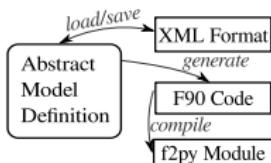
MJH and K Reuter, Top. Catal. 57, 159 (2014)

Multi-lattice kMC



MJH, M Scheffler, K Reuter, (in preparation) 2014.

General kMC code **kmos**



MJH, S Matera, K Reuter, Comp. Phys. Commun. 185, 2138, (2014).

Outlook

- construct transition pathway for surface oxide formation
- finally elucidate character of active surface on Pd(100)