Beat the Heat!

First-principles based modeling of micro- and macroscopic heat dissipation in heterogeneous catalysis

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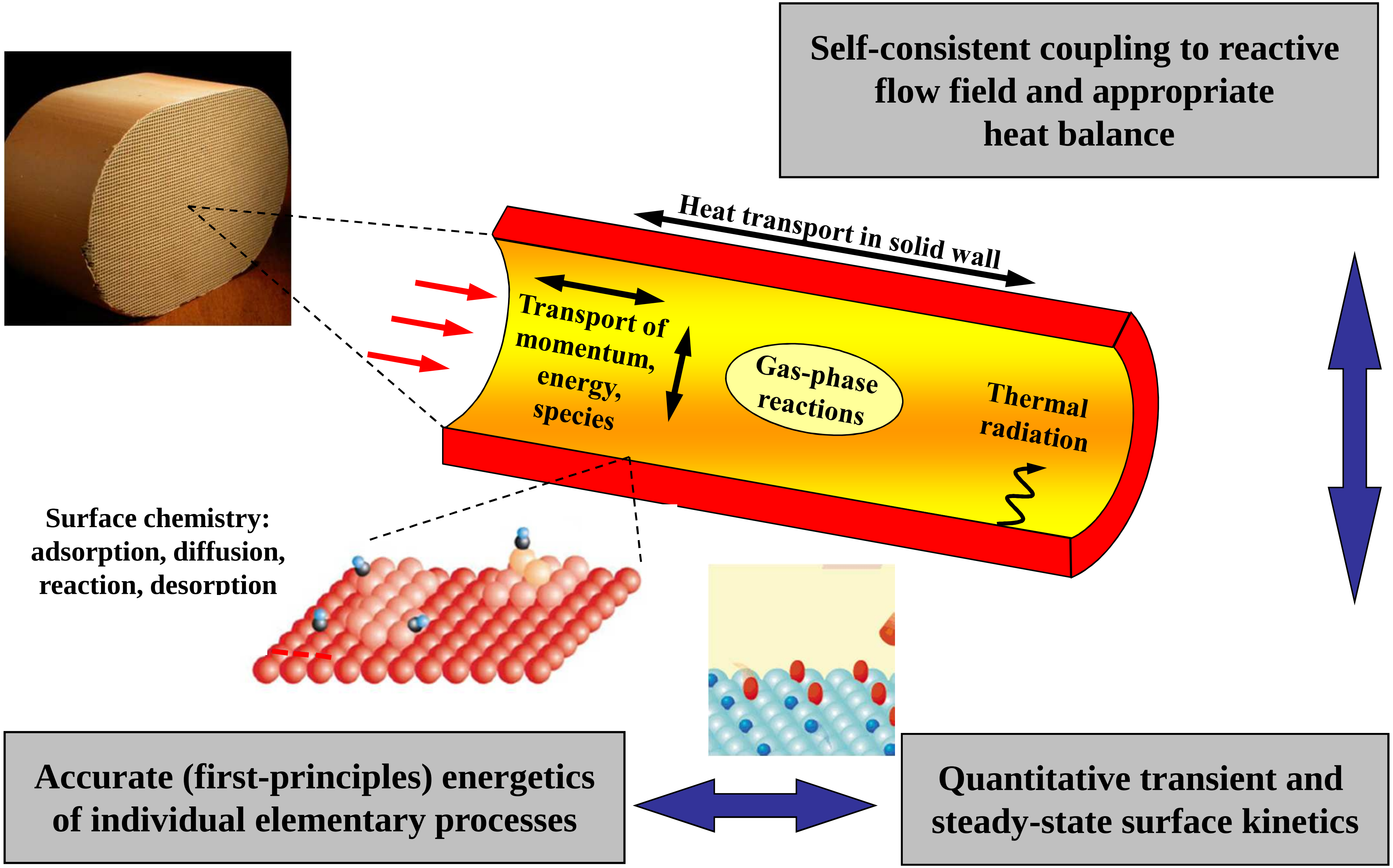
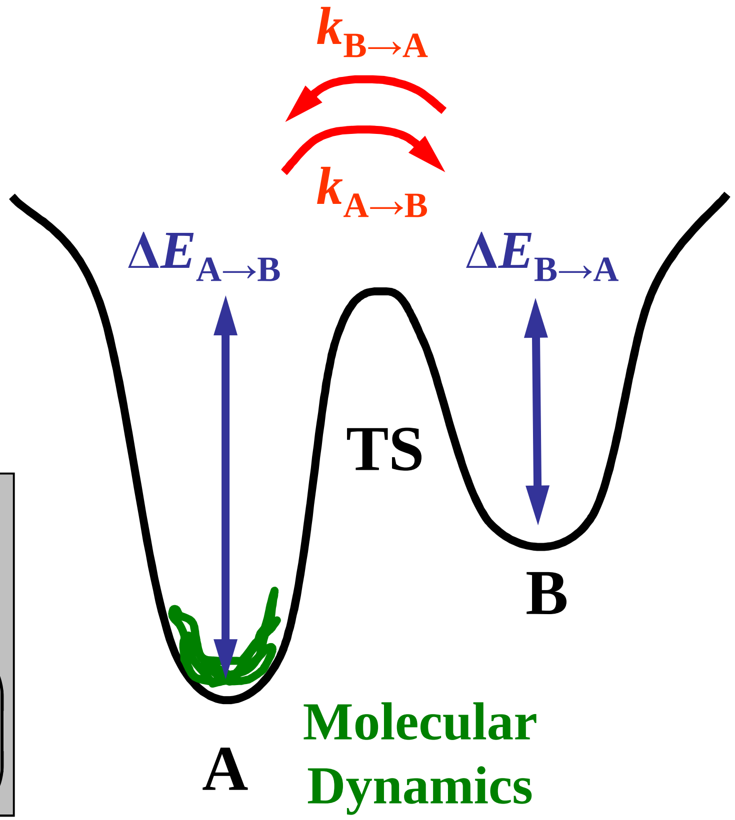
Challenges across the scales



I. Integrating first-principles microkinetics into fluid dynamical simulations:

Macroscopic heat dissipation

Chemical kinetics: Tackling rare-event time scales

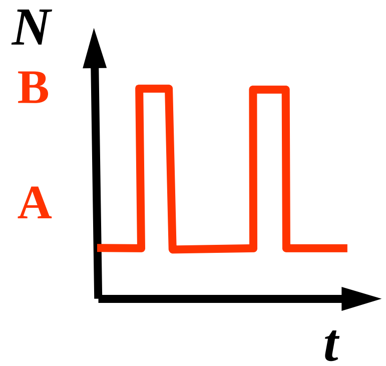


Transition State Theory

$$k_{i\to j} = \left(\frac{k_B T}{h}\right)\frac{Z_{TS(i\to j)}}{Z_i}$$

$$= \Gamma_\circ \exp\left(\frac{-\Delta E_{i\to j}}{k_B T}\right)$$

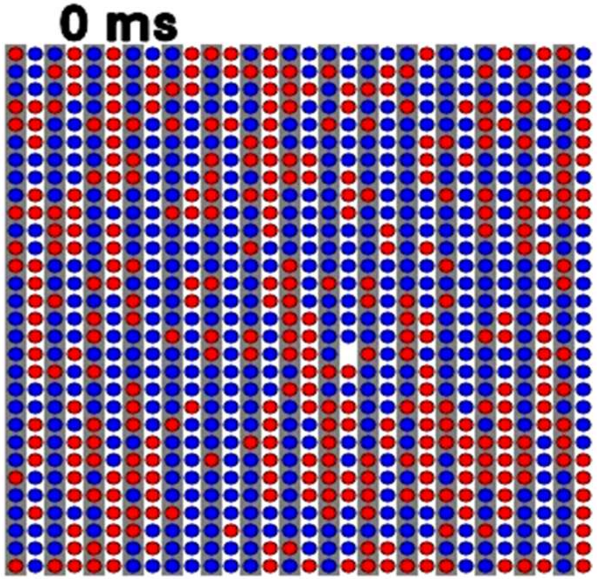
kinetic Monte Carlo



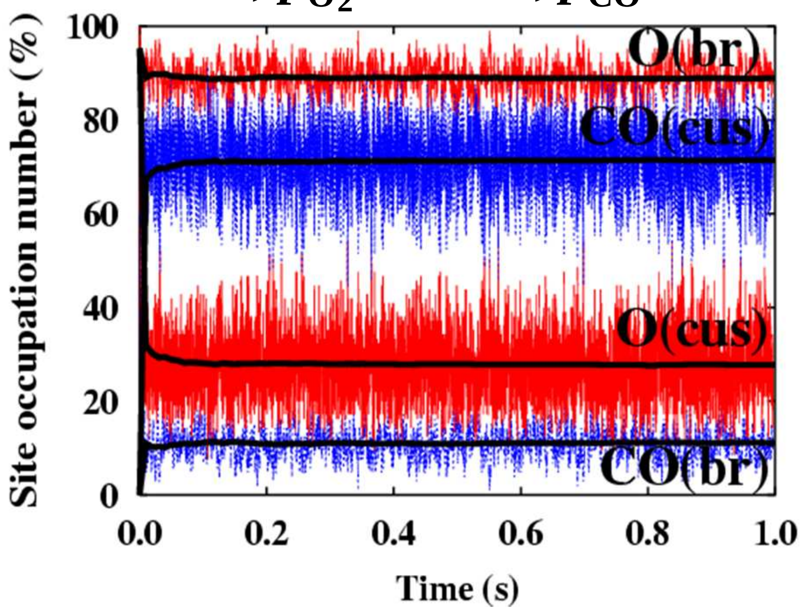
$$\frac{dP_i(t)}{dt} = -\sum_j k_{i\to j} P_i(t) + \sum_j k_{j\to i} P_j(t)$$

First-principles kinetic Monte Carlo simulations for heterogeneous catalysis: Concepts, status and frontiers
K. Reuter, in "Modeling Heterogeneous Catalytic Reactions: From the Molecular Process to the Technical System", (Ed.) O. Deutschmann, Wiley-VCH, Weinheim (2011). http://www.th4.ch.tum.de

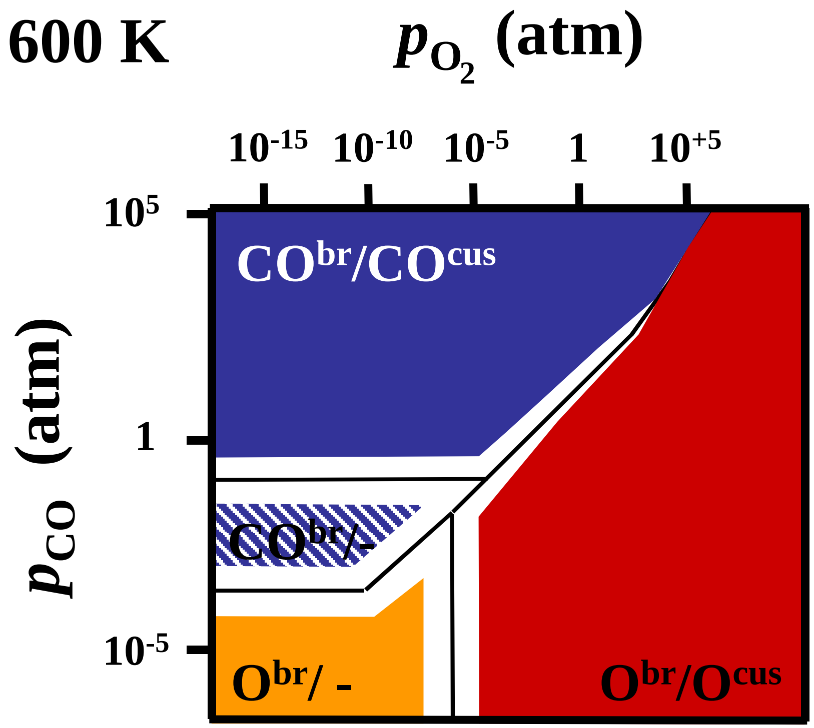
Surface structure and composition in the reactive environment



T = 600 K, p_{O_2} = 1 atm, p_{CO} = 7 atm

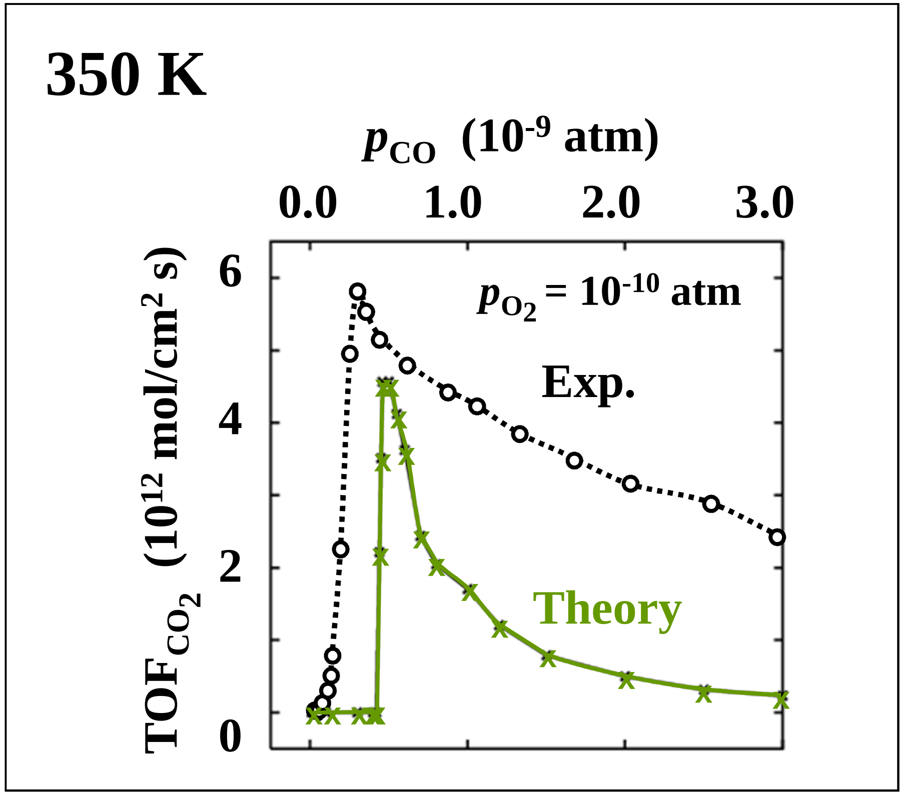


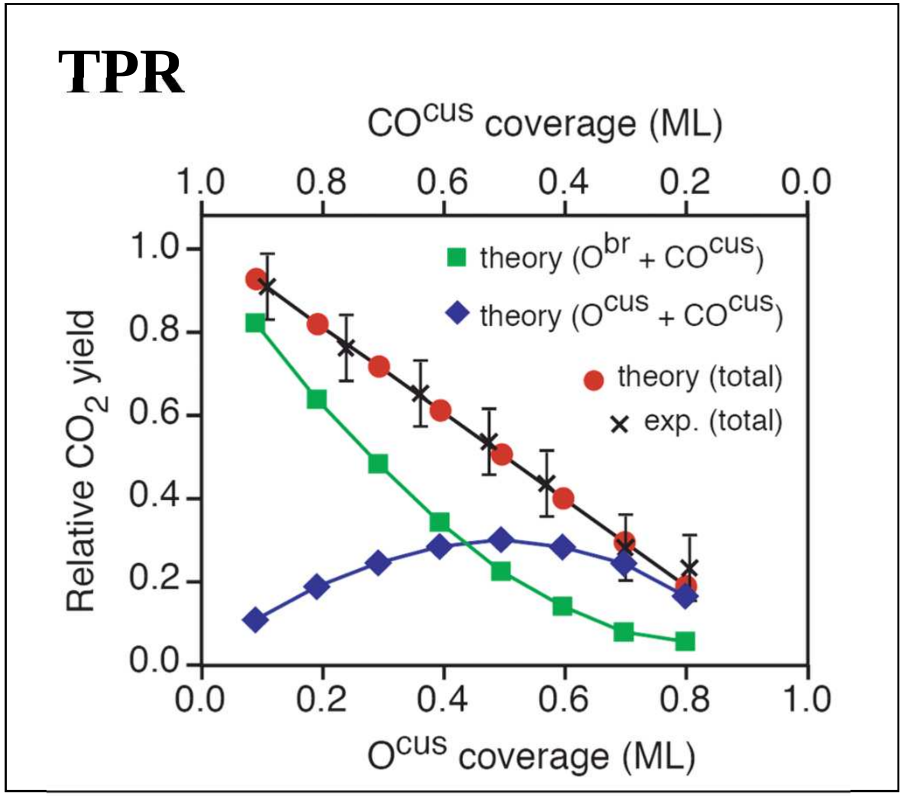
CO oxidation at $RuO_2(110)$



K. Reuter, D. Frenkel and M. Scheffler,
Phys. Rev. Lett. 93, 116105 (2004)

Steady-state and transient parameter-free turnover frequencies



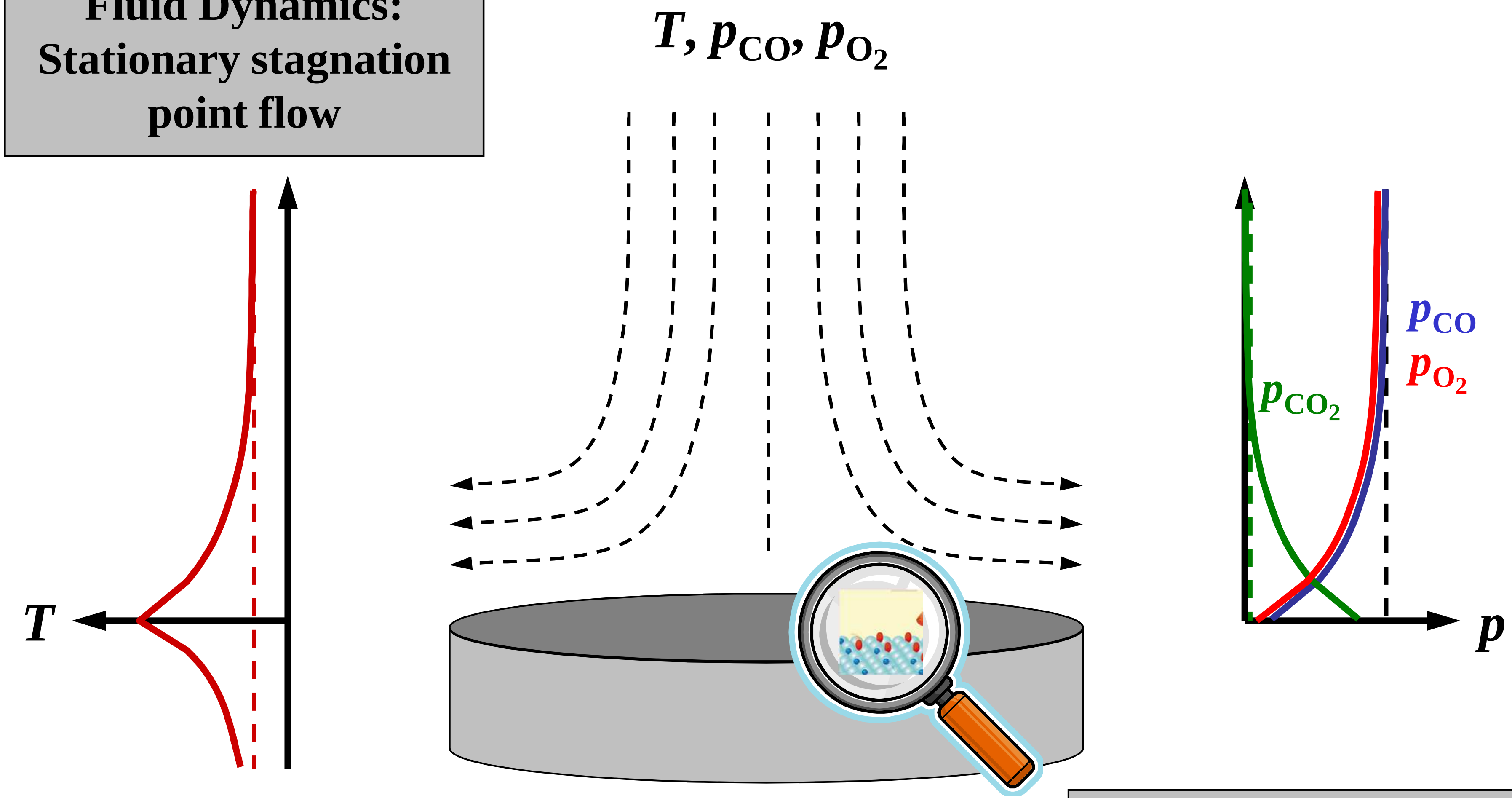


K. Reuter and M. Scheffler,
Phys. Rev. B 73, 045433 (2006)

M. Rieger, J. Rogal, and K. Reuter,
Phys. Rev. Lett. 100, 016105 (2008)

Macroscopic regime: Heat and mass transfer

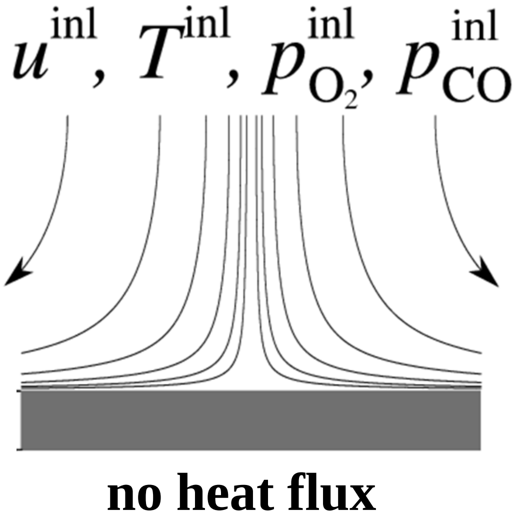
Computational Fluid Dynamics: Stationary stagnation point flow

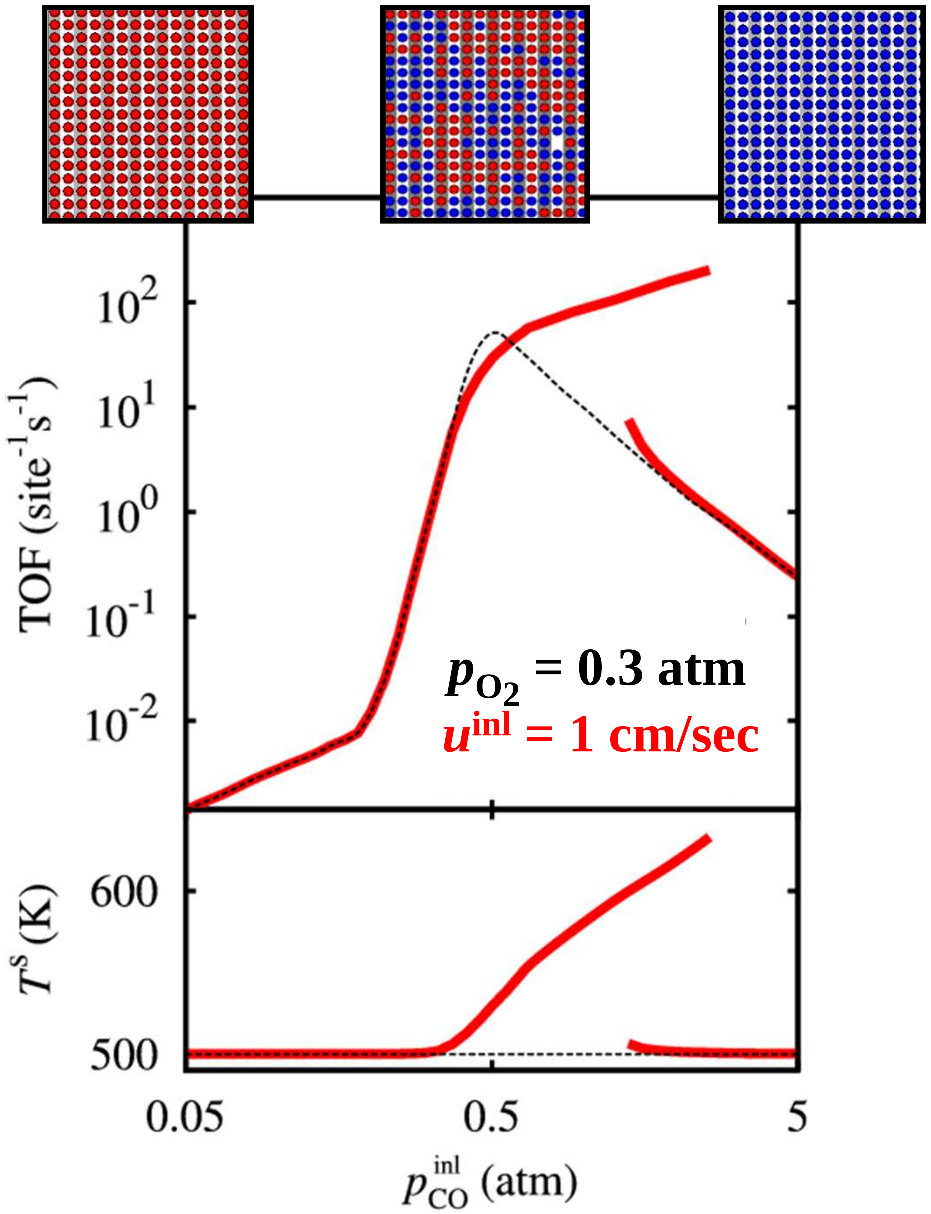


Chemical source terms from 1p-kMC

S. Matera and K. Reuter, Phys. Rev. B 82, 085446 (2010)

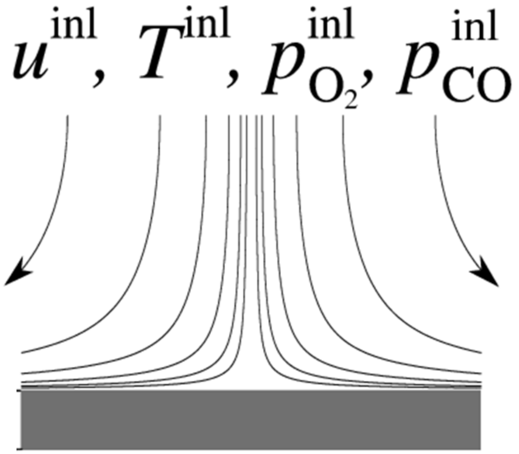
Adiabatic limit: Surface heating



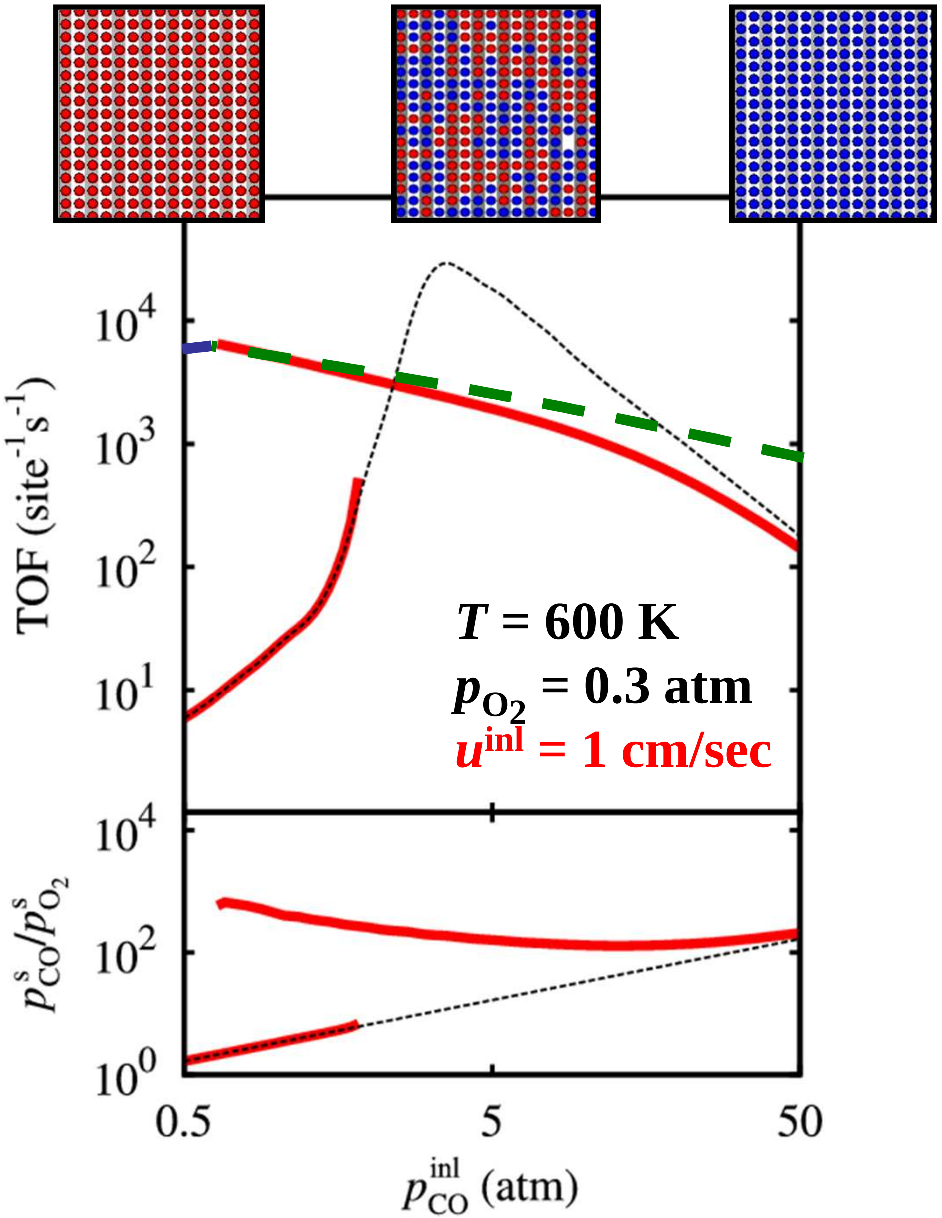


S. Matera and K. Reuter, Catal. Lett. 133,156 (2009)

Isothermal limit: Mass transfer limitations

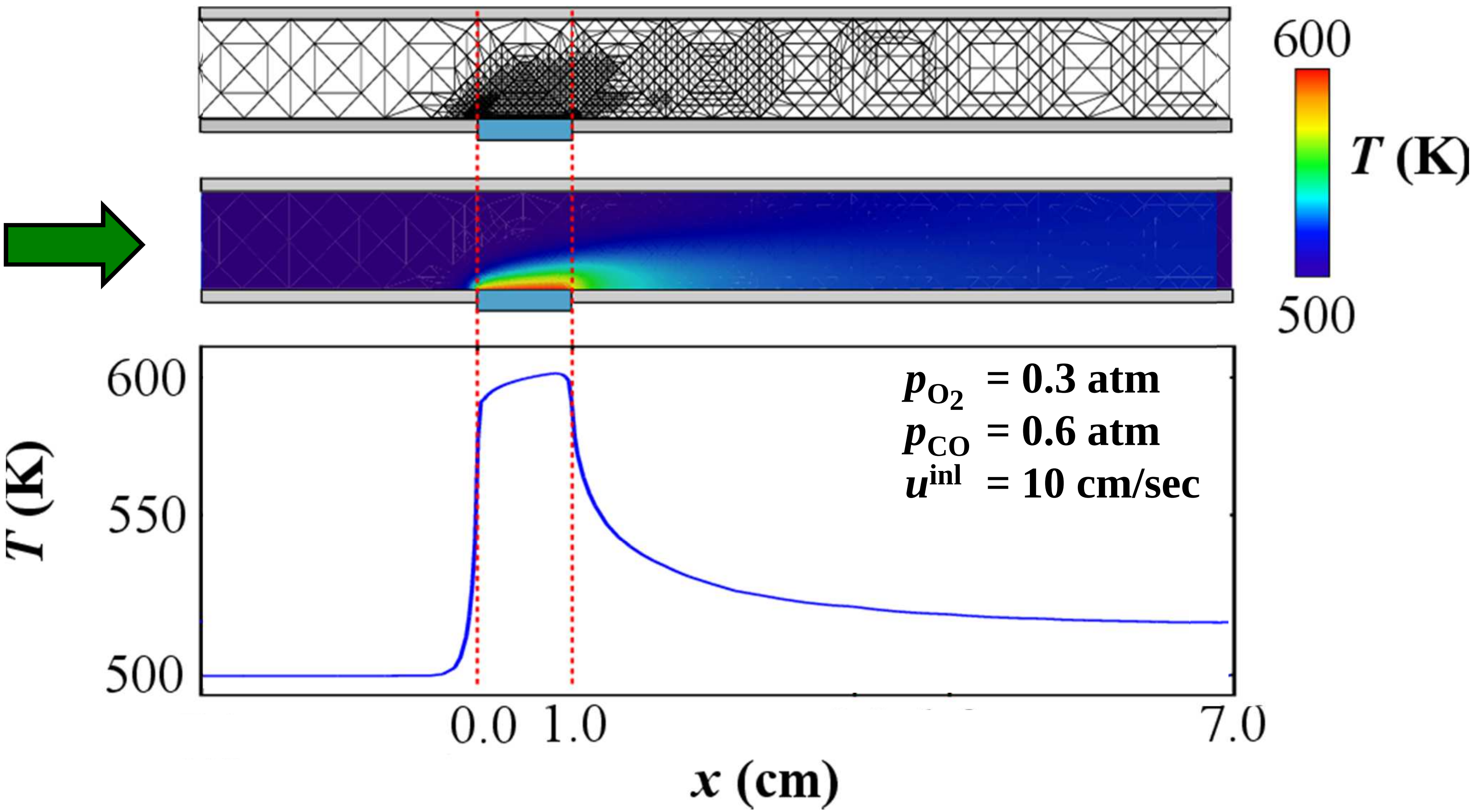


***T* = const**



S. Matera and K. Reuter, Catal. Lett. 133, 156 (2009)

Lateral channel flow: Surface heating and spatial variations

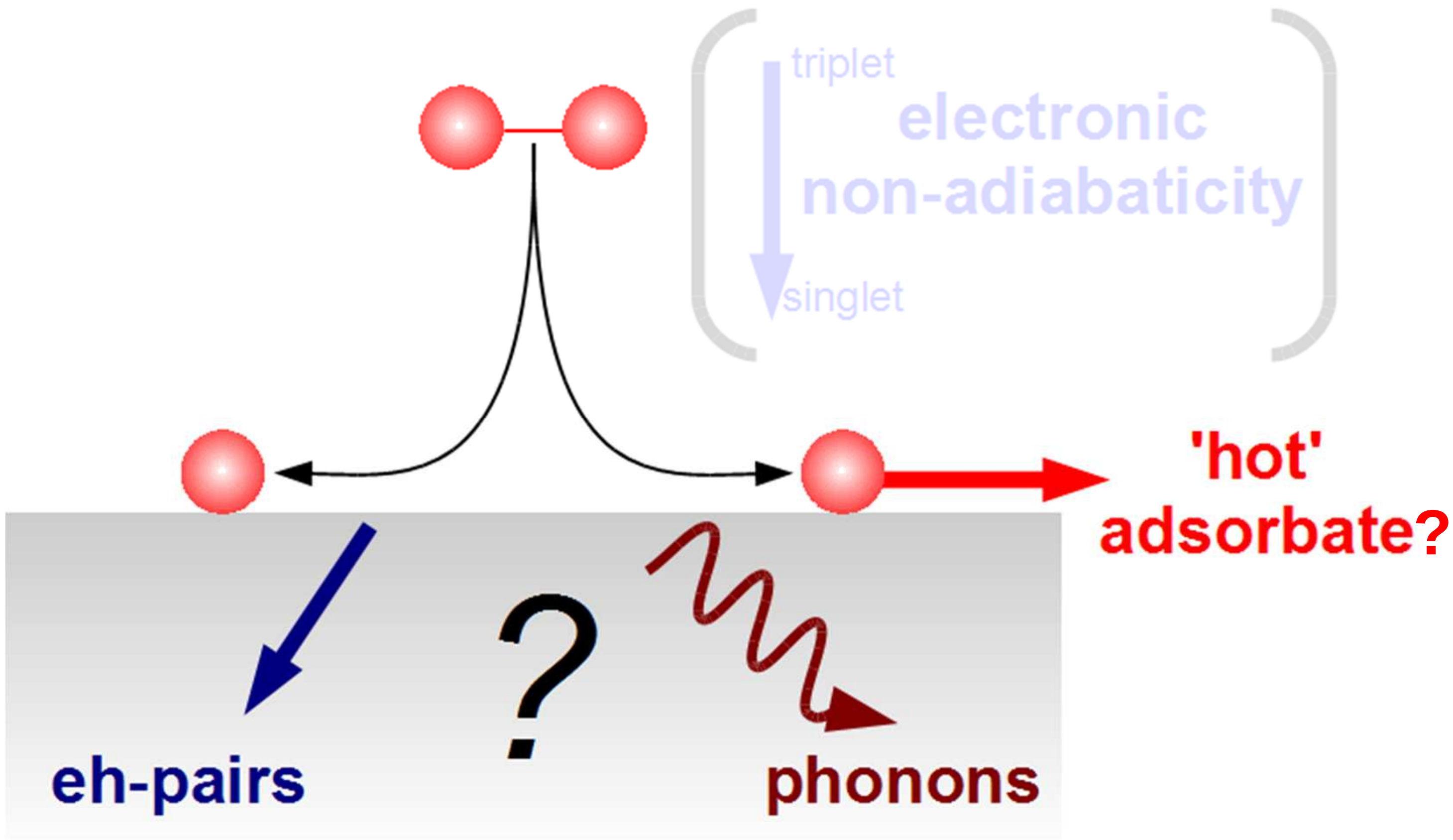


S. Matera and K. Reuter, in preparation

II. Heat dissipation:

More than just macroscale warm-up?!

Really Markov ?!



Showcase O_2/Pd(100):	2.6eV adsorption energy released ! (at GGA/PBE level)

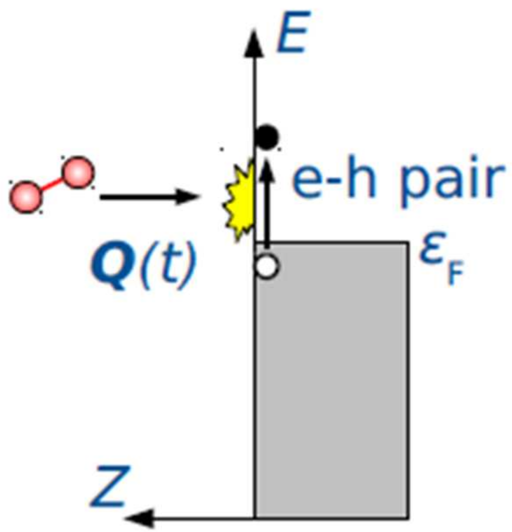
e-h pair excitation: Time-dependent perturbation theory

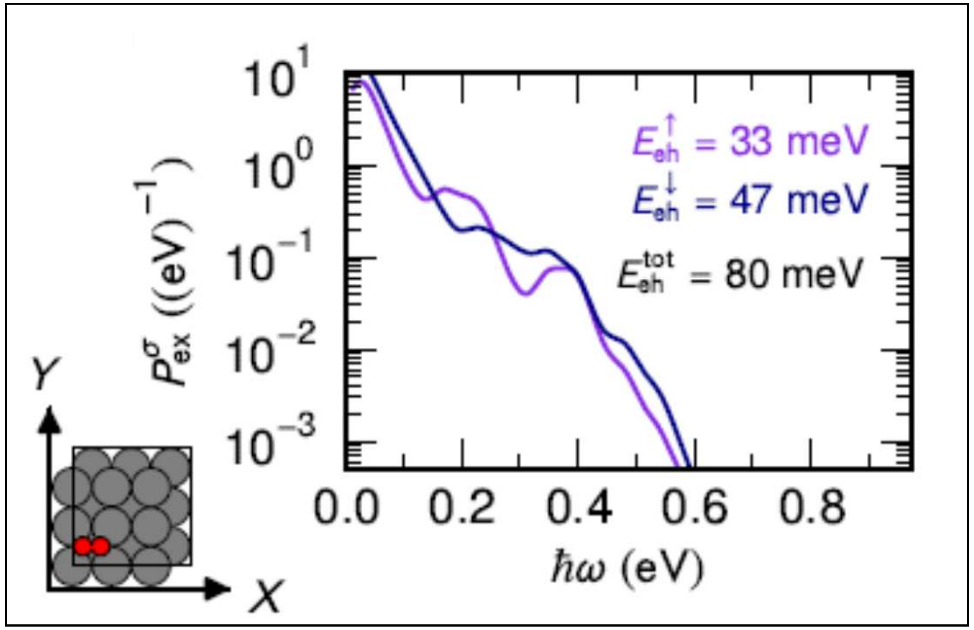
$$\boxed{h^\sigma(t) \approx h_{(0)} + v^\sigma(Q(t))}$$

M. Timmer and P. Kratzer, Phys. Rev. B 79, 165407 (2009)

$$p_{ij}^\sigma(t) = \frac{1}{i\hbar} \langle \varepsilon_j^\sigma | v^\sigma(Q(t)) | \varepsilon_i^\sigma \rangle \exp\left(\frac{i}{\hbar} (\varepsilon_j^\sigma - \varepsilon_i^\sigma)\, t \right)$$

$$\tilde{P}_{\mathrm{ex}}^\sigma(\hbar\omega) = \sum_{ij} \left| \int_{-\infty}^{+\infty} \mathrm{d}t\, p_{ij}(t) \right|^2 \delta\left(\hbar\omega - (\varepsilon_j^\sigma - \varepsilon_i^\sigma)\right) \qquad E_{\mathrm{eh}}^\sigma = \int_0^{+\infty} \mathrm{d}\varepsilon\, \varepsilon\, P_{\mathrm{ex}}^\sigma(\varepsilon)$$





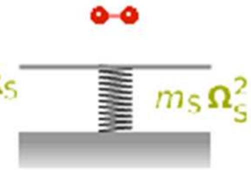
J. Meyer and K. Reuter, New J. Phys. 13, 085010 (2011)

Phonon energy sinks „from the shelf“

- surface oscillator (SO) J. C. Polanyi and R. J. Wolf, *J. Chem. Phys.* **82**, 1555 (1985).

☺ easily coupled to frozen surface potential: $V_{6D}^{SO} = V_{6D}(\mathbf{R}_{6D} - \mathbf{R}_S) + \frac{1}{2} m_S \, \mathbf{R}_S \, \mathbf{\Omega}_S^2 \, \mathbf{R}_S$

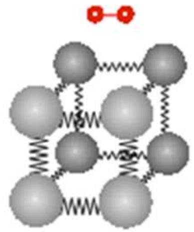
☹ minimalistic Einstein approximation for substrate degrees of freedom



- generalized Langevin equations J. C. Tully, *J. Chem. Phys.* **73**, 1975 (1980).

☺ in principle large bath included in ansatz: $H = H_{\text{bath}} + H_{\text{sys}} + H_{\text{int}}$

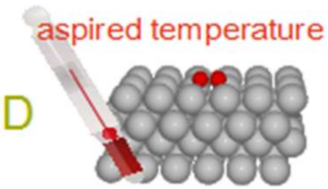
☹ ***but:*** in practice harmonic solid **and** approximations when integrating out bath degrees of freedom



- thermostats e.g. M. E. Tuckerman and G. J. Martyna, *J. Phys. Chem. B* **104**, 159 (2000).

☺ modified EOM allowing to sample ***NVT*** statistical properties via MD

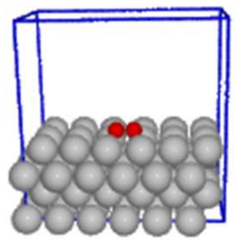
☹ ***but:*** single trajectories lose physical meaning



- *ab-initio* MD (AIMD) e.g. A. Groß, *Phys. Rev. Lett.* **103**, 246101 (2009).

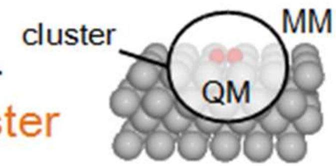
☺ substrate mobility described at *ab-initio* quality

☹ affordable supercell sizes (**PBC**s!) limits description of phonons

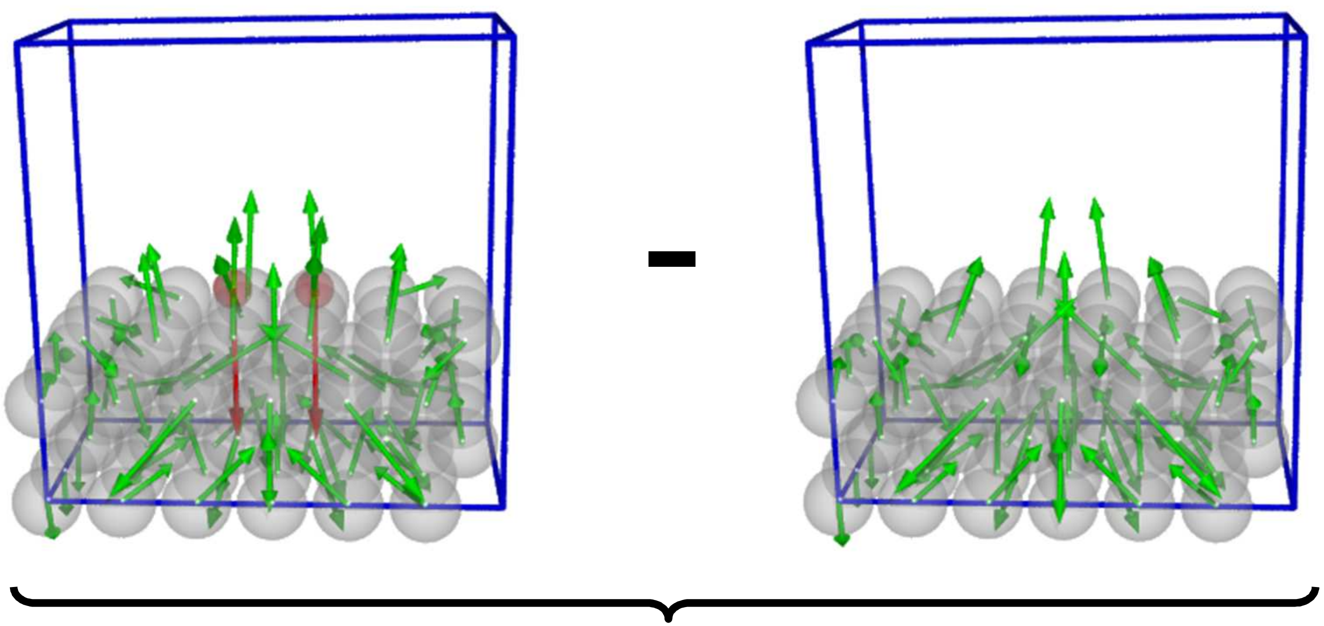


- QM/MM embedding e.g. C. Bo and F. Maseras, *Dalton Trans.* **2911** (2008).

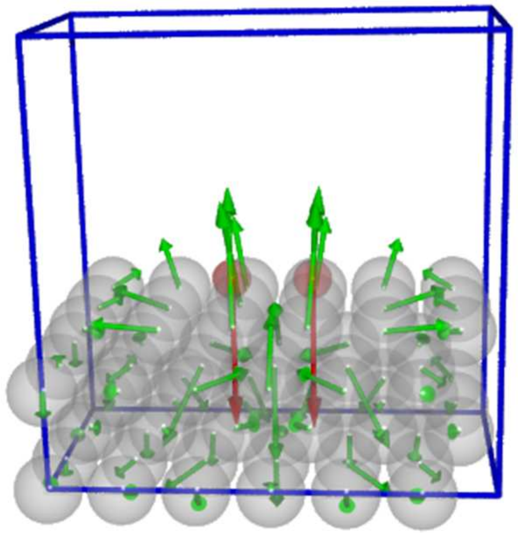
☹ metallic band structure cannot be mimicked by feasibly large cluster

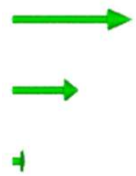


Exploiting locality: Elastic vs. chemical forces



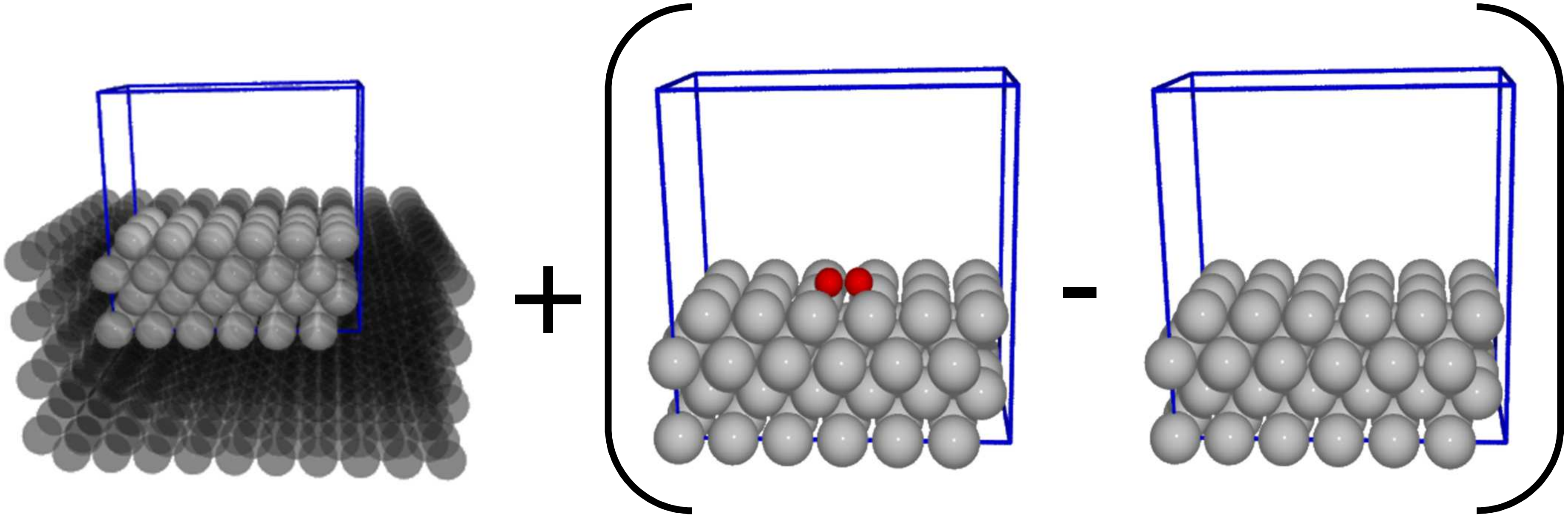
Adsorbate-induced forces very short ranged !





forces (eV/Å)
1.0
0.1
0.01

QM/Me embedding



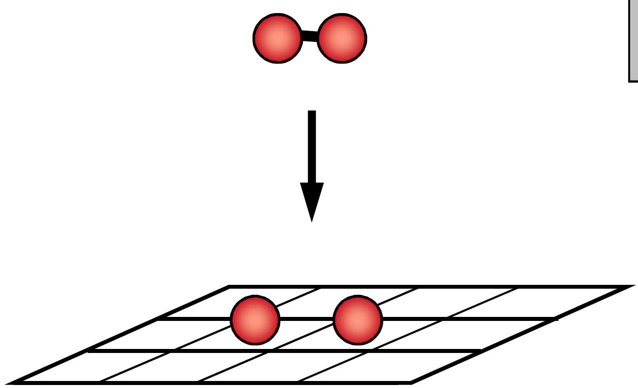
Large-scale MM MD … with additional QM-force contributions

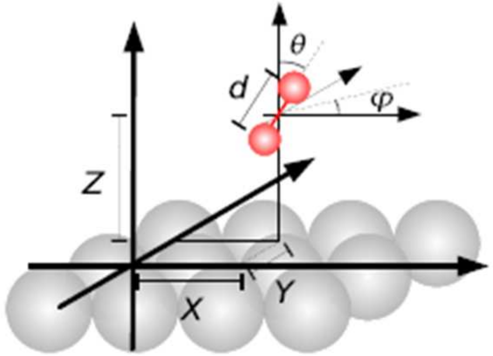
DFT-parametrized MEAM
50x50x50 Pd atoms
LAMMPS
S. J. Plimpton, J. Comp. Phys. 117, 1 (1995)

DFT GGA/PBE
6x3x4 (or 8x3x4) slabs
CASTEP
S.J. Clark *et al.*, Z. Kristallogr. 220, 567 (2005)

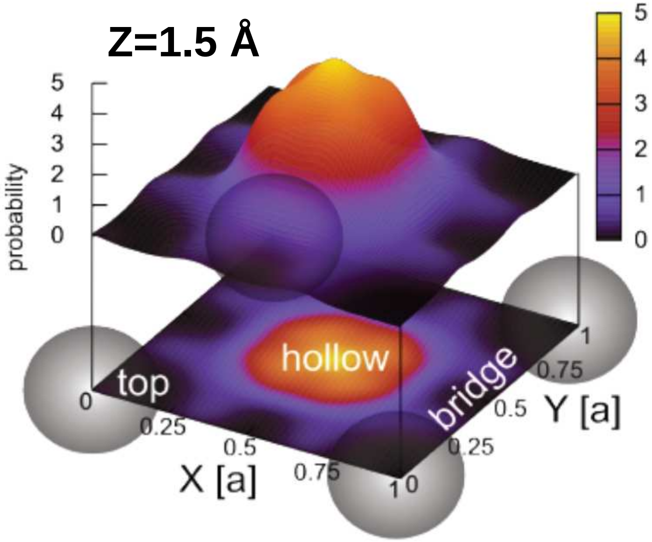
Forget Markov: Hot adatoms are alive!

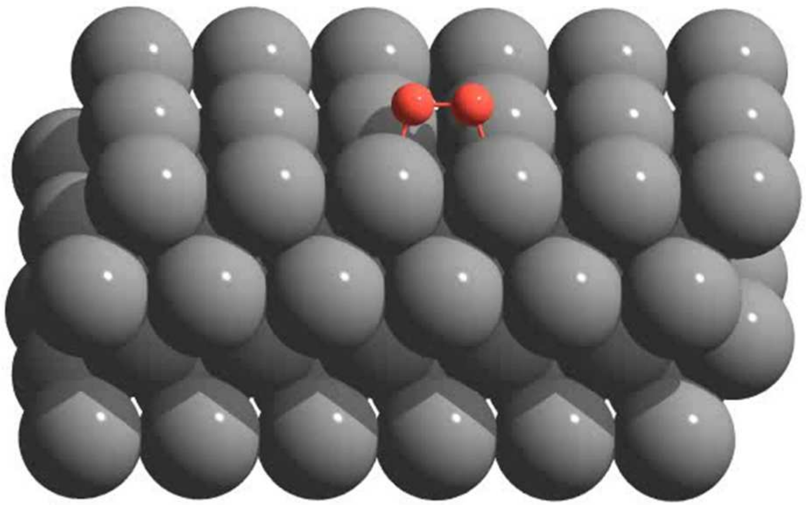
$$k = \tilde{S}_{\circ}(T)\frac{pA_{\mathrm{uc}}}{\sqrt{2\pi m k_{\mathrm{B}} T}}$$





$$V_{\mathrm{fsa}} = (X, Y, Z, d, \theta, \varphi)$$

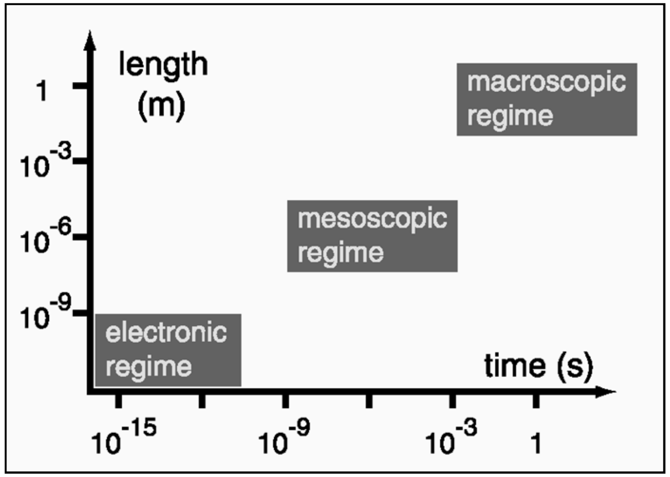




J. Meyer and K. Reuter, submitted

Beaten by the heat…

Detailed account of heat dissipation at macroscopic and microscopic level essential to reach predictive-quality in comprehensive (nano!) catalysis modeling



Sebastian Matera

Jörg Meyer