Bridging the Pressure Gap (in Theory…)

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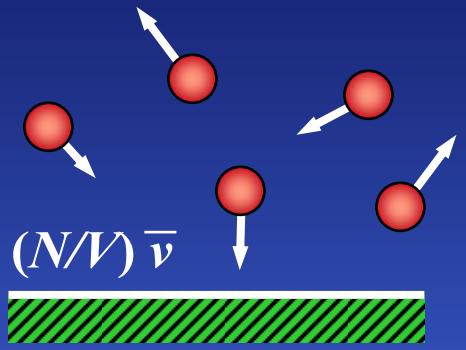
Impingement and the "Surface Science" Ansatz



$$Z = \frac{p}{(2\pi mkT)^{1/2}}$$

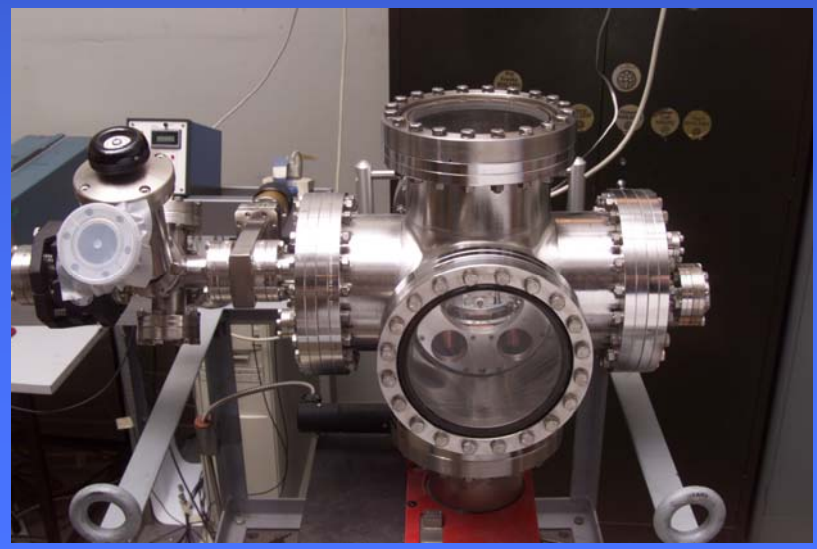
10^{15} sites/cm^2, T=300 K,

p = 1 atm: $Z \sim 10^8$ site^{-1} s^{-1} !!

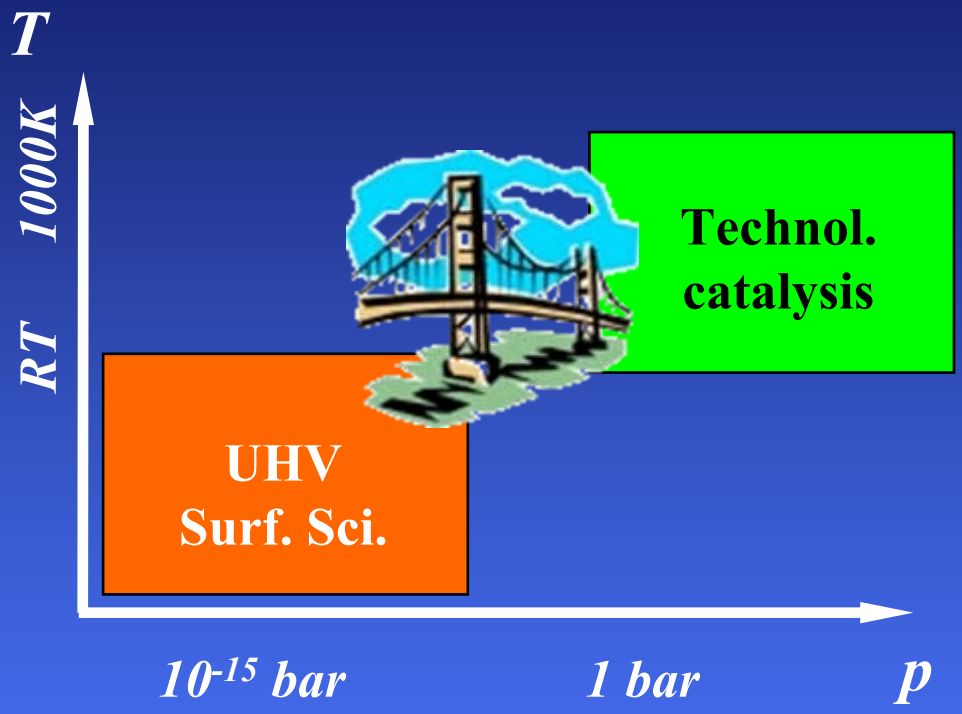
Requires $p \lesssim 10^{-12}$ atm to keep a "clean" surface clean for $t \sim 1h$

Surface Science:

- $T \rightarrow$ 0K, UHV
- no equilibrium with gas phase
- deposition at fixed dosage
  (1 Langmuir = 10^{-6} Torr s $\approx 10^{-9}$ atm s)
  - Many techniques developed that only work in UHV („*ex situ*")



Pressure / Materials Gap in Heterogeneous Catalysis



Pressure gap:

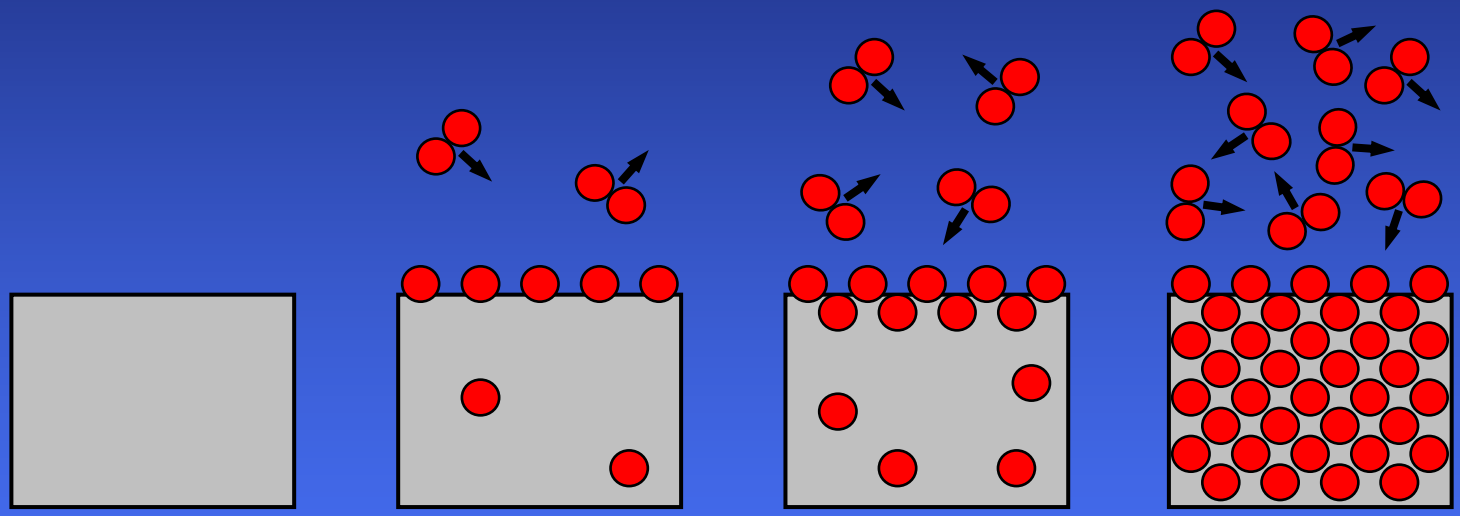
Low vs. high temperatures

Finite dosage vs. gas phase reservoir

Materials (Complexity) gap:

Low-index single crystal surfaces vs. supported nanoparticles

Example: Oxide Formation in Oxidation Catalysis



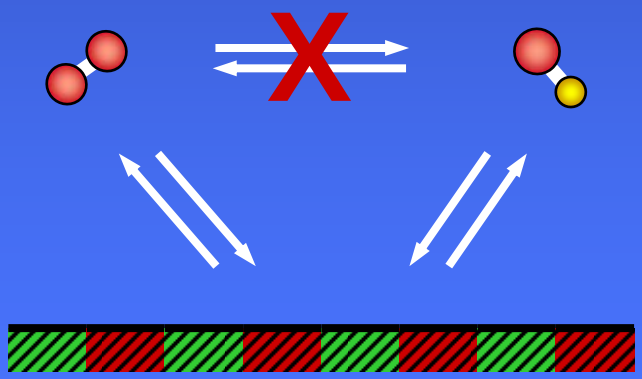
Nanometer and sub-nanometer thin oxide films at surfaces of late transition metals,
K. Reuter, in: Nanocatalysis: Principles, Methods, Case Studies,
(Eds.) U. Heiz, H. Hakkinen, and U. Landman, Springer (Berlin, 2006)
http://www.fhi-berlin.mpg.de/th/paper.html

Bridging the (Pressure) Gap

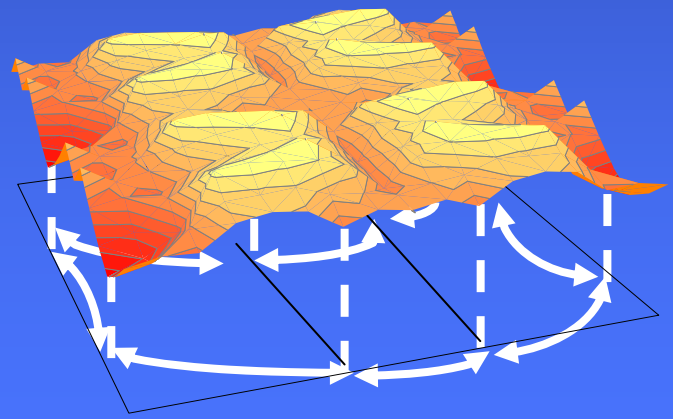
Experiment: - Awareness and diligent experiments…
- Development and use of „*in situ*“ techniques

Theory: - Development and use of
first-principles statistical mechanics approaches

„Constrained Equilibrium“
Atomistic Thermodynamics

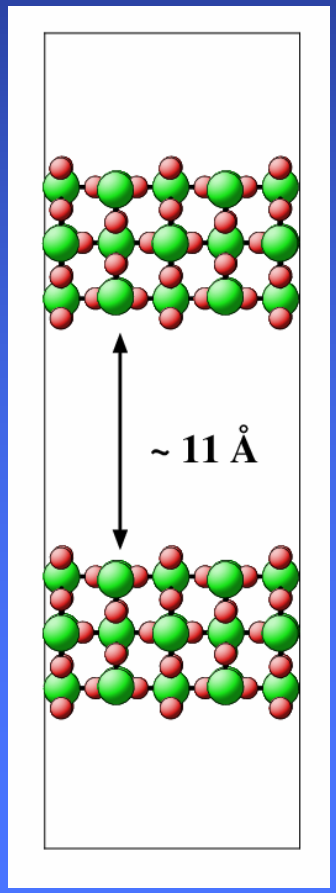


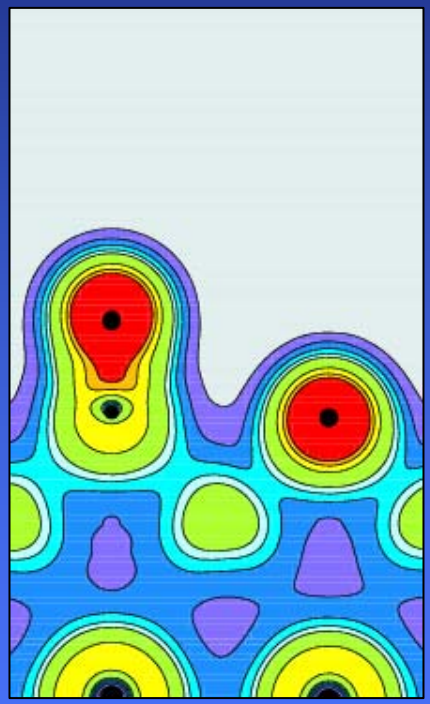
Kinetic Monte Carlo
Simulations

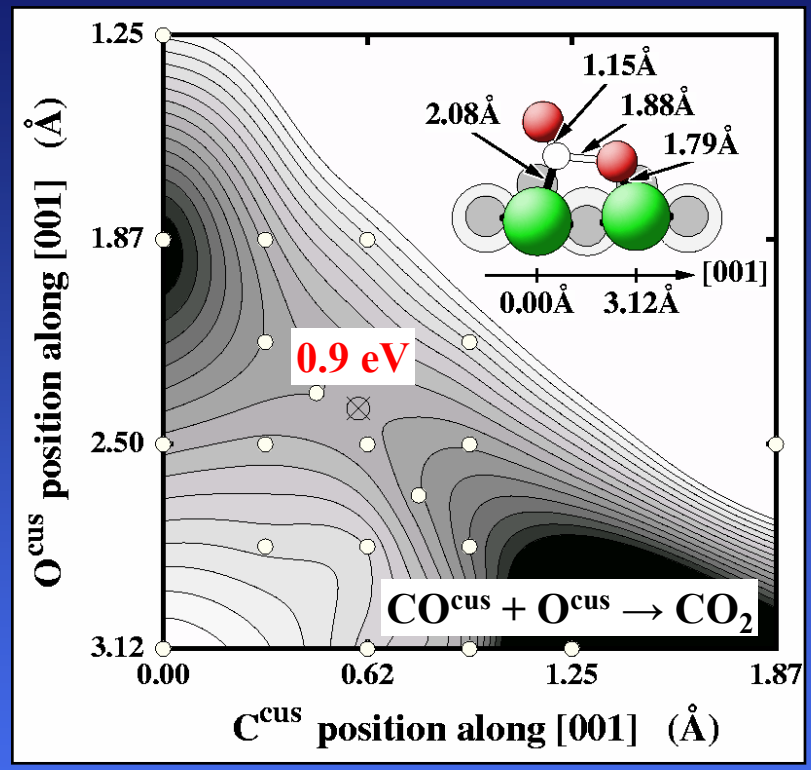


1. The Electronic Regime

DFT for Surface Chemical Reactions

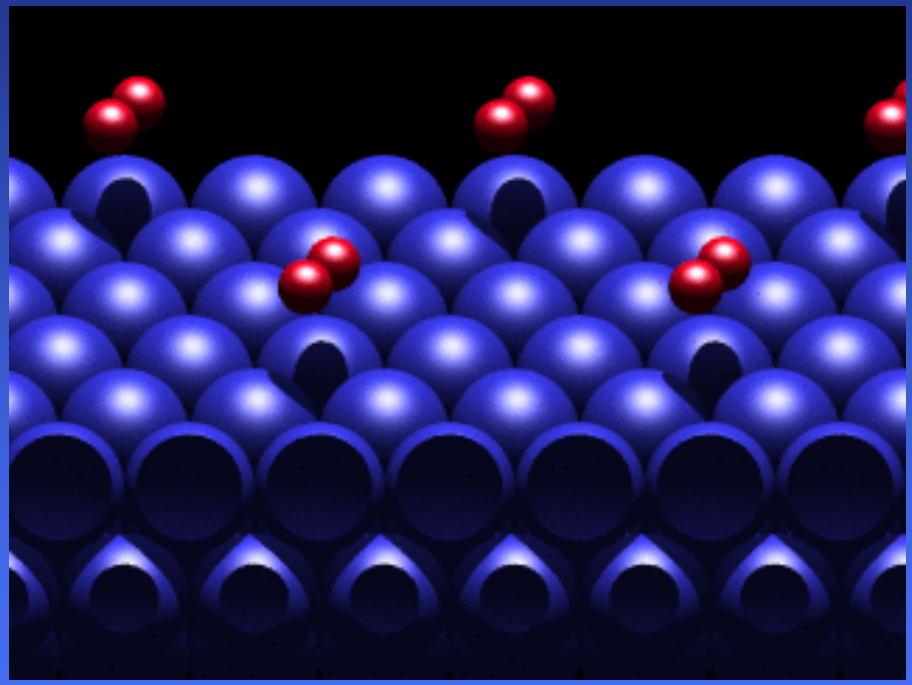






- Total energy
- Forces (relaxation, vibrations, MD…)
- Electronic structure (…)

Keeping Everything: Expensive, Limited Time Scale



J. Behler *et al.*, Phys. Rev. Lett. 94, 036104 (2005)

Example:

O_2 dissociation at Al(111)

Total time of trajectory: 0.5 ps
Time step: 2.5 fs (200 steps)

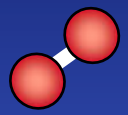
CPU cost: 45 days on
1 Compaq
ES45 processor

2. Effect of a Surrounding Gas Phase on the Surface Structure and Composition: Equilibrium

Ab initio atomistic thermodynamics for surfaces: A primer, J. Rogal and K. Reuter, RTO-AVT-142, VKI Lecture Series on "Experiment, Modeling and Simulation of Gas-Surface Interactions for Reactive Flows in Hypersonic Flights", Rhode-St-Genèse, Belgium (2006). http://www.fhi-berlin.mpg.de/th/paper.html

First-Principles Atomistic Thermodynamics

$\mu_{O_2}(T, p)$



equilibrium

$$G(T, p) = E^{\text{tot}} + F^{\text{vib}} - TS^{\text{conf}} + pV$$

DFT

C.M. Weinert and M. Scheffler,
Mater. Sci. Forum 10-12, 25 (1986);
E. Kaxiras *et al.*, Phys. Rev. B 35, 9625 (1987)

Computation of Free Energies: Ideal Gas I

$$Z = 1/N! \left(\cancel{Z_{nucl}}\ Z_{el}\ Z_{trans}\ Z_{rot}\ Z_{vib} \right)^N$$

$$\Rightarrow \quad \mu(T,p) = G / N = (F + pV) / N = (- k_B T \ln(Z) + pV) / N$$

i) Electr. free energy $\quad Z_{el} = \sum_i \exp(-E_i^{el} / k_B T)$

$$\Rightarrow F_{el} \approx E^{tot} - k_B T \ln(I_{spin})$$

Typical excitation energies eV >> $k_B T$, only (possibly degenerate) ground state contributes significantly

Required input: Internal energy E^{tot}
Ground state spin degeneracy I_{spin}

ii) Transl. free energy $\quad Z_{trans} = \sum_{\underline{k}} \exp(-\hbar k^2 / 2mk_B T)$ $\quad$ Particle in a box of length $L = V^{1/3}$

$$(L \to \infty) \quad \Rightarrow \quad Z_{trans} \approx V (2\pi mk_B T / \hbar^2)^{3/2}$$

Required input: Particle mass m

Computation of Free Energies: Ideal Gas II

iii) Rotational free energy $Z_{rot} = \sum_J (2J+1)\exp(-J(J+1)B_0 / k_B T)$ Rigid rotator

(Diatomic molecule) $\Rightarrow Z_{rot} \approx -k_B T \ln(k_B T/\sigma B_0)$ $\sigma = 2$ (homonucl.), $= 1$ (heteronucl.)
$B_0 \sim md^2$ (d = bond length)

Required input: Rotational constant B_0
(exp: tabulated microwave data)

iv) Vibrational free energy $Z_{vib} = \sum_{i=1}^{M} \sum_n \exp(-(n + \tfrac{1}{2})\hbar\omega_i / k_B T)$ Harmonic oscillator

$$\Rightarrow \mu_{vib}(T) = \sum_{i=1}^{M} \tfrac{1}{2}\hbar\omega_i + k_B T \ln(1 - \exp(-\hbar\omega_i/k_B T))$$

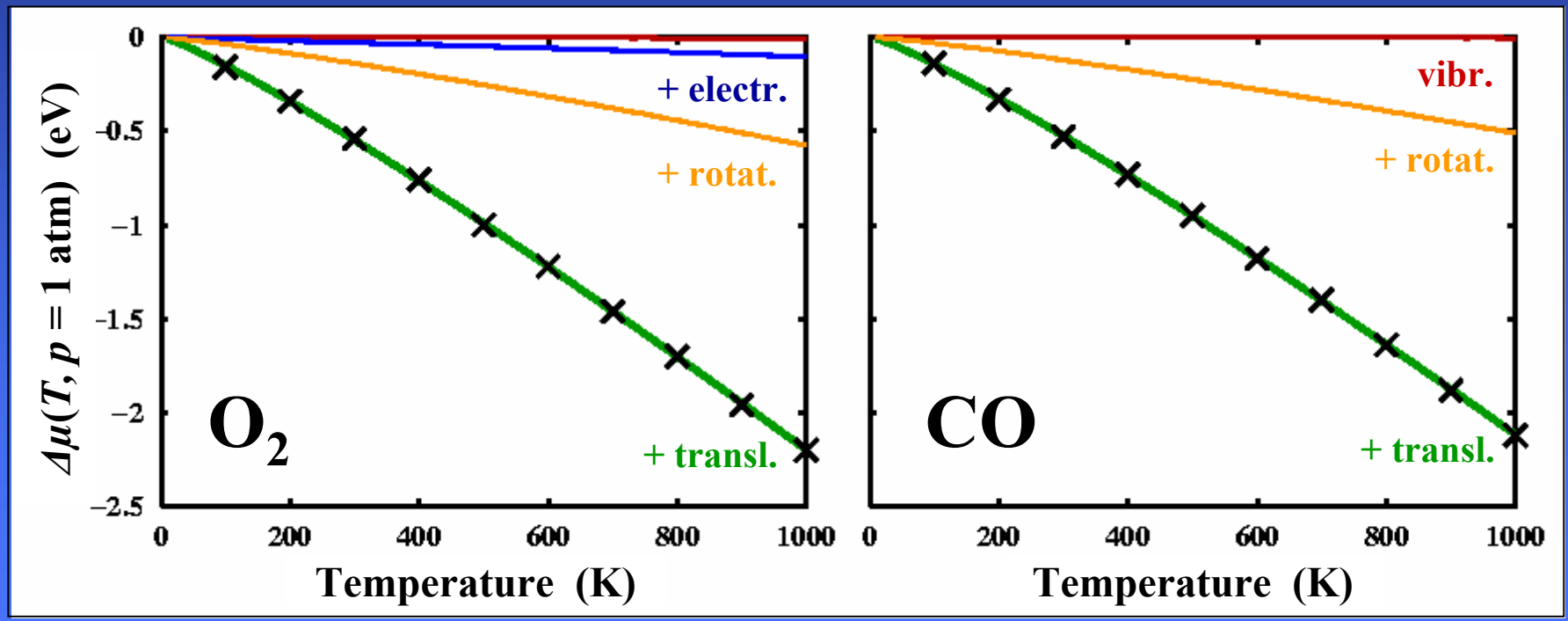
Required input: M fundamental vibr. modes ω_i

Calculate dynamic matrix $D_{ij} = (m_i m_j)^{-1/2} (\partial^2 E^{tot}/\partial r_i \partial r_j)_{r_{eq}}$
Solve eigenvalue problem $\det(D - 1\ \omega_i^2)$

Computation of Free Energies: Ideal Gas III

		O_2	CO
m	(amu)	32	28
$\nu_{stretch}$	(meV)	196	269
B_o	(meV)	0.18	0.24
σ		2	1
I_{spin}		3	1

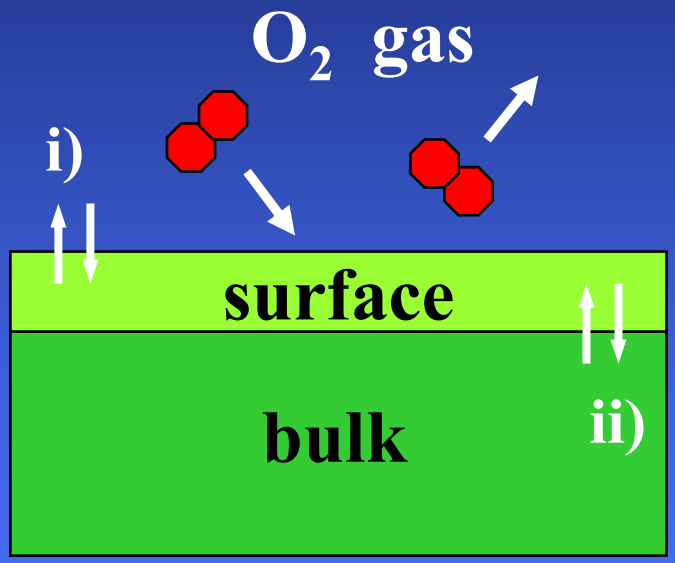
$$\mu = \mu(T,p) = E^{tot} + \Delta\mu(T,p)$$



Alternatively: $\Delta\mu(T, p) = \Delta\mu(T, p^o) + kT \ln(p/p^o)$
and $\Delta\mu(T, p^o = 1\ atm)$ tabulated in thermochem. tables (e.g. JANAF)

Example: Surface in Contact with Oxygen Gas Phase

$$\gamma_{\text{surf.}} = 1/A \left[G_{\text{surf.}}(N_O, N_M) - N_O \mu_O - N_M \mu_M \right]$$



Use reservoirs:

i) μ_O from ideal gas

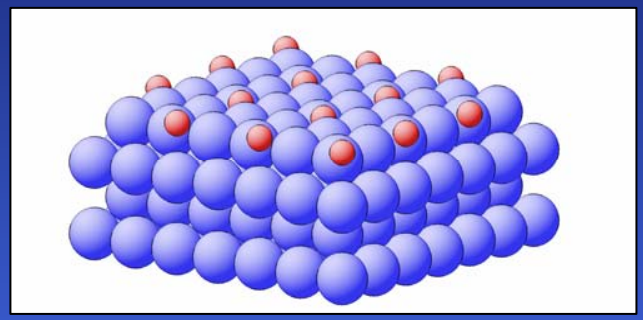
ii) $\mu_M = g_M^{\text{bulk}}$

Forget about F^{vib} and F^{conf} for the moment:

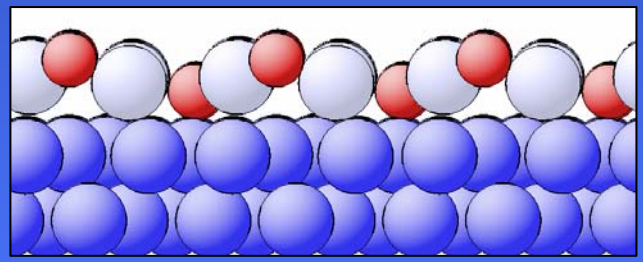
$$\gamma(T,p) \approx \left(E_{\text{surf.}}^{(\text{slab})} - N_M E_M^{\text{bulk}} \right)/A - N_O \mu_O(T,p)/A$$

Oxide formation on Pd(100)

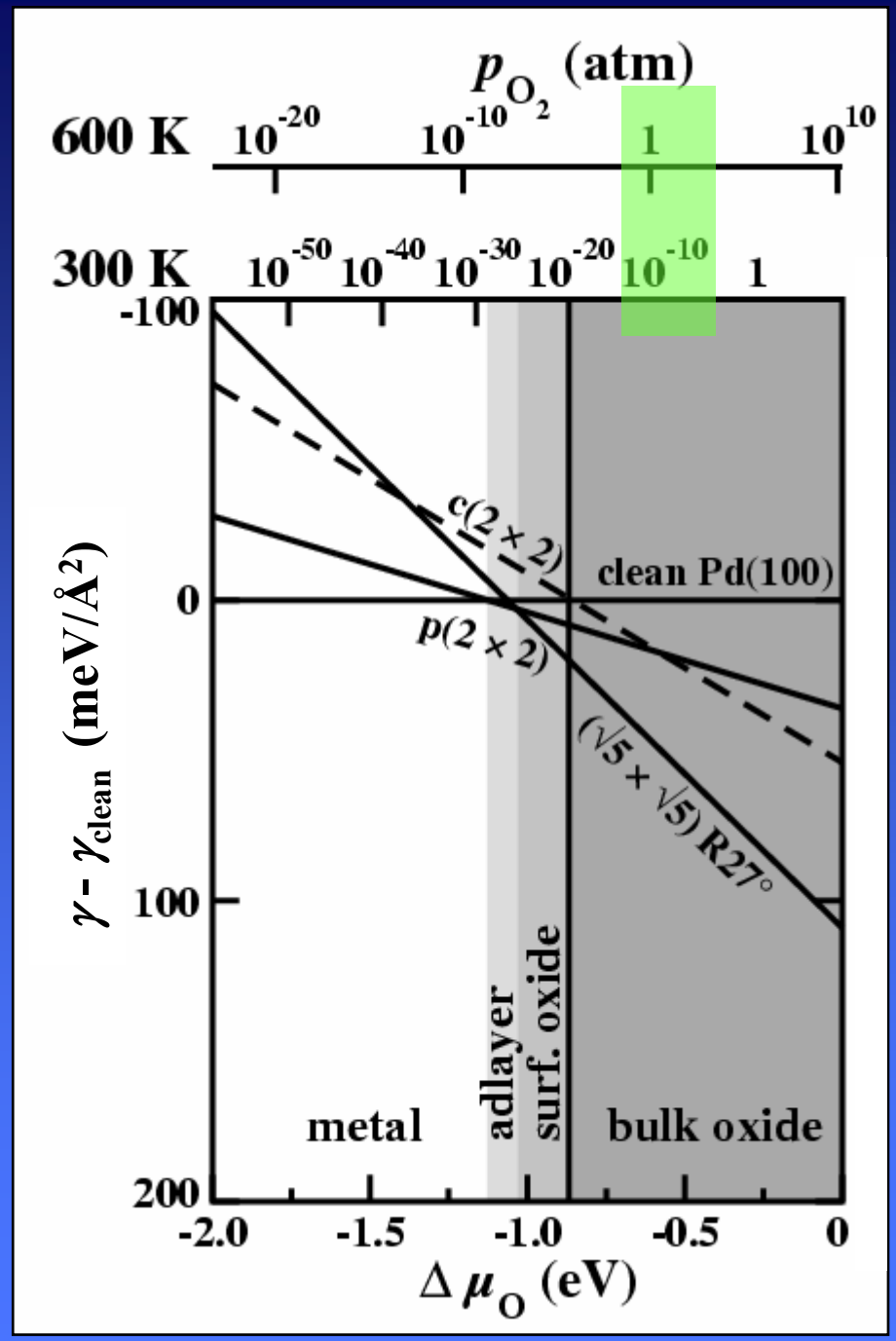
$$\gamma \approx \left(E_{\text{surf.}}^{(\text{slab})} - N_{\text{M}} E_{\text{M}}^{\text{bulk}} \right)/A \; - \; N_{\text{O}} \mu_{\text{O}}/A$$



p(2x2) O/Pd(100)

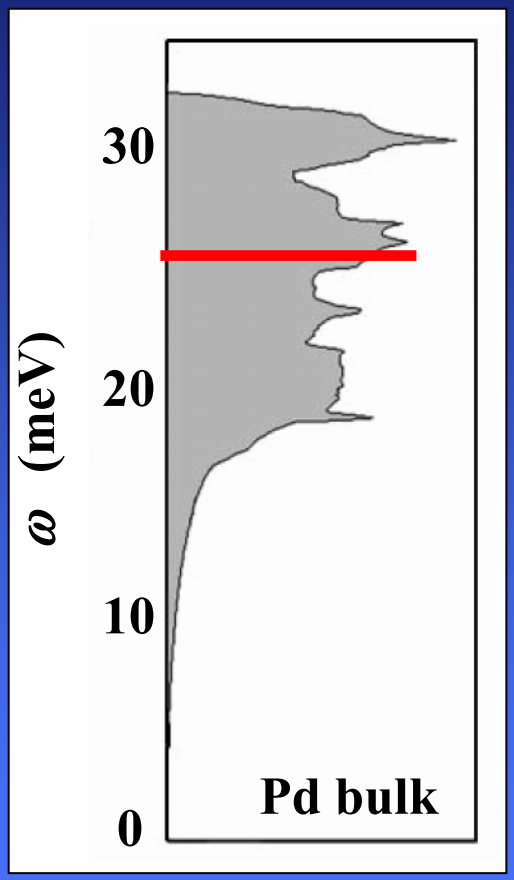


($\sqrt{5} \times \sqrt{5}$)*R27°* PdO(101)/Pd(100)



M. Todorova *et al.*, Surf. Sci. 541, 101 (2003);
K. Reuter and M. Scheffler,
Appl. Phys. A 78, 793 (2004)

Vibrational Contributions to the Surface Free Energy



$$F^{vib}(T,V) = \int d\omega\, F^{vib}(T,\omega)\, \sigma(\omega)$$

$$\Rightarrow \quad \gamma^{vib} = \Delta F^{vib}/A =$$

$$= 1/A \int d\omega\, F^{vib}(T,\omega) \left[\sigma^{surf.}(\omega) - N_{Ru}\sigma^{bulk}(\omega)\right]$$

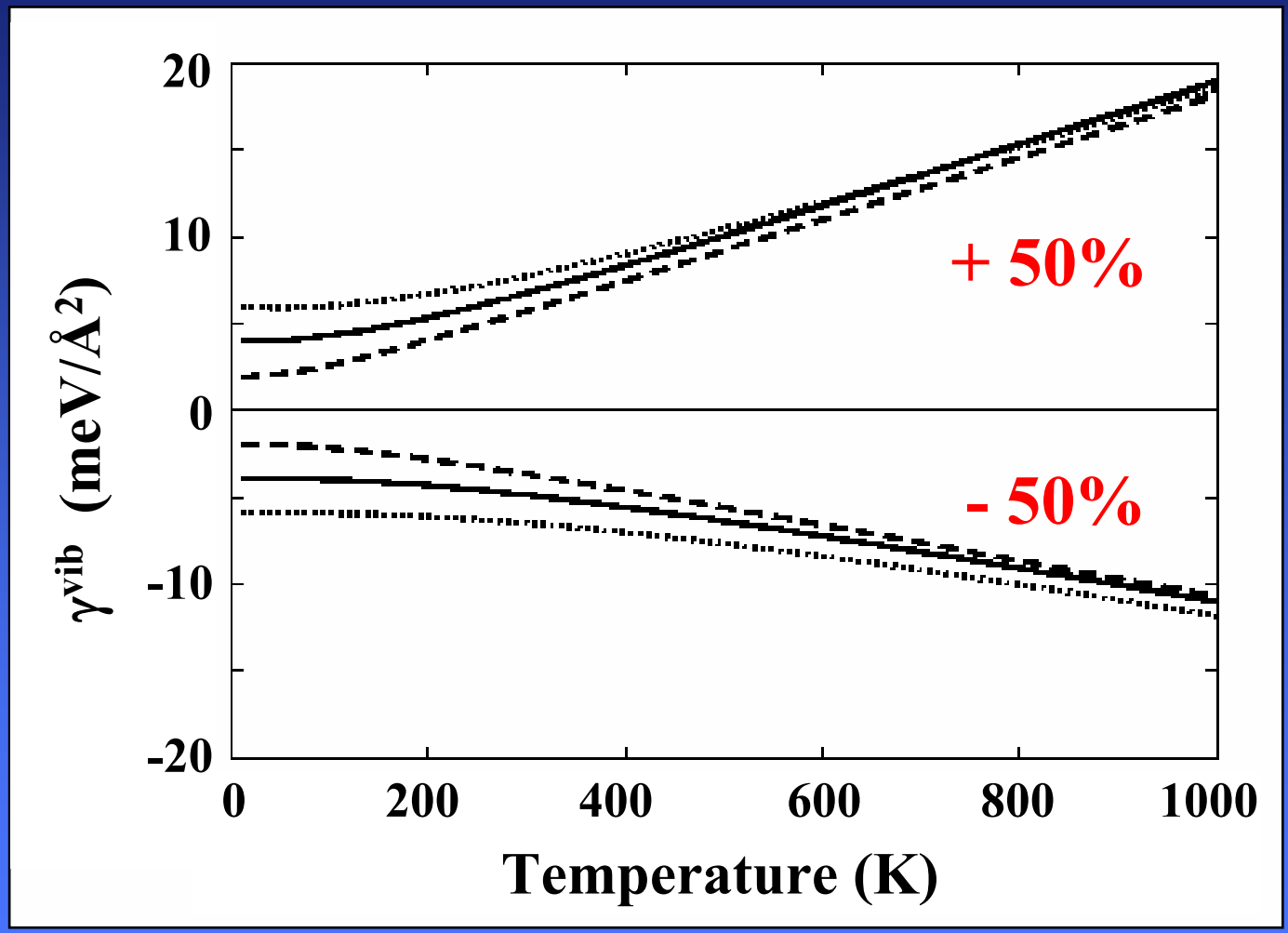
Only the vibrational changes at the surface contribute to the surface free energy

$\Rightarrow$ **Use simple models for order of magnitude estimate**

e.g. Einstein model: $\sigma(\omega) = \delta(\omega - \underline{\omega})$

$\underline{\omega}_{Pd}$**(bulk) ~ 25 meV**

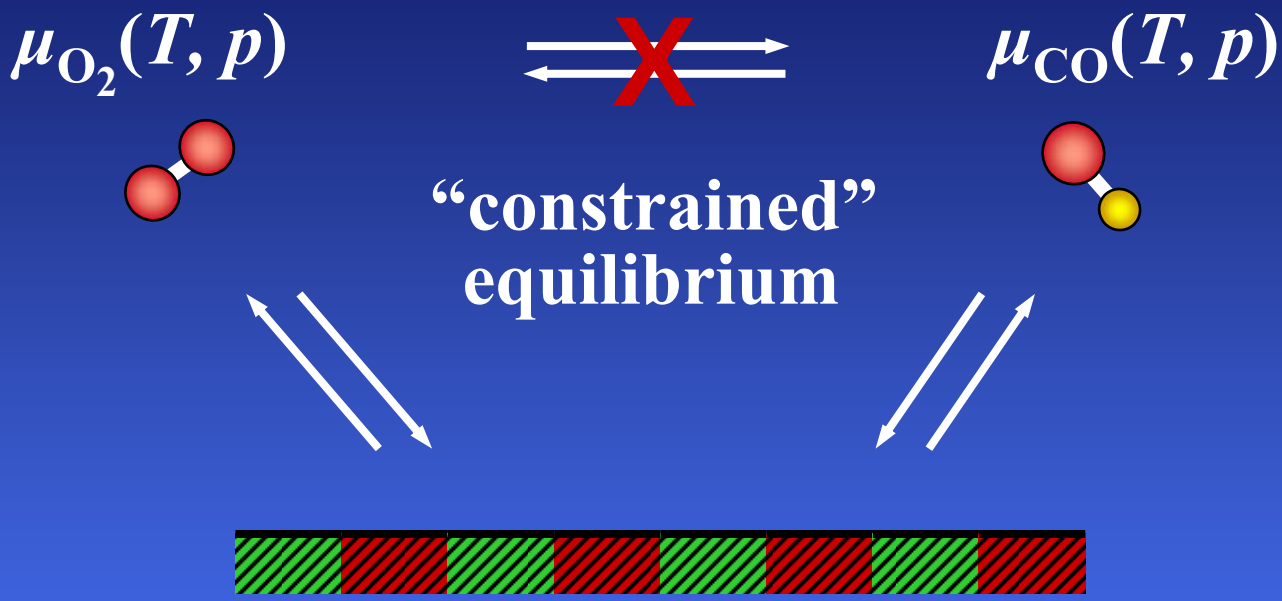
Surface Induced Variations of Substrate Modes



< 10 meV/Å^2 for T < 600 K - in this case!!!

3. Towards Catalysis: "Constrained Equilibria"

First-Principles Atomistic Thermodynamics



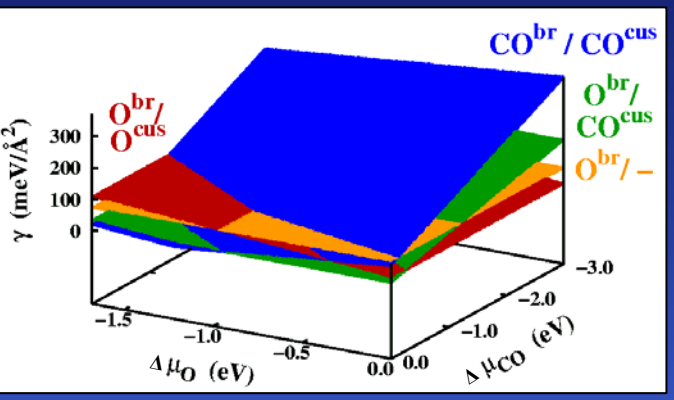
$$G(T, p) = E^{\text{tot}} + F^{\text{vib}} - TS^{\text{conf}} + pV$$

DFT

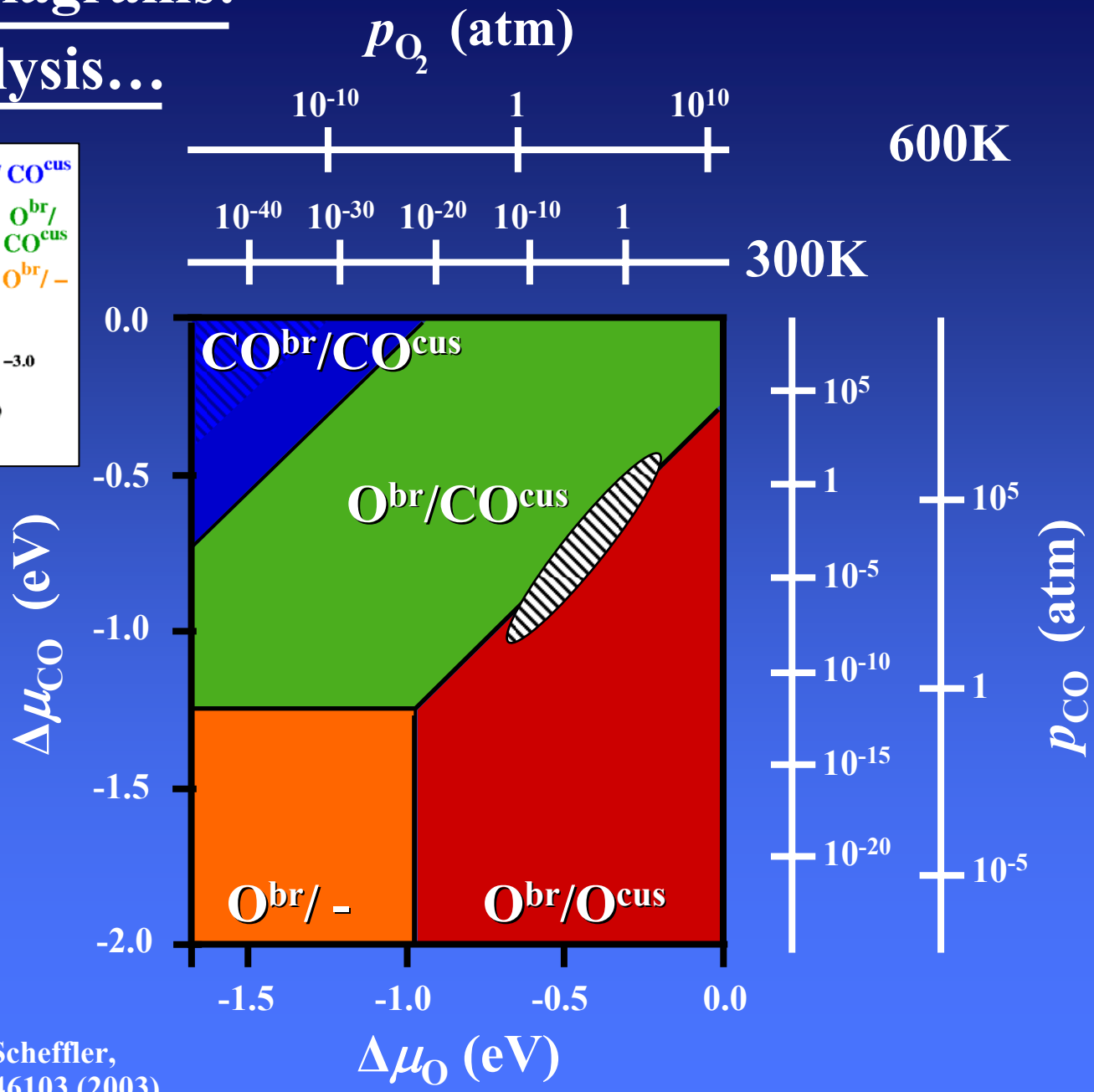
C.M. Weinert and M. Scheffler, Mater. Sci. Forum 10-12, 25 (1986); E. Kaxiras *et al.*, Phys. Rev. B 35, 9625 (1987)

K. Reuter and M. Scheffler, Phys. Rev. B 65, 035406 (2001); Phys. Rev. B 68. 045407 (2003)

Surface phase diagrams: towards catalysis…



CO Oxidation at $RuO_2(110)$

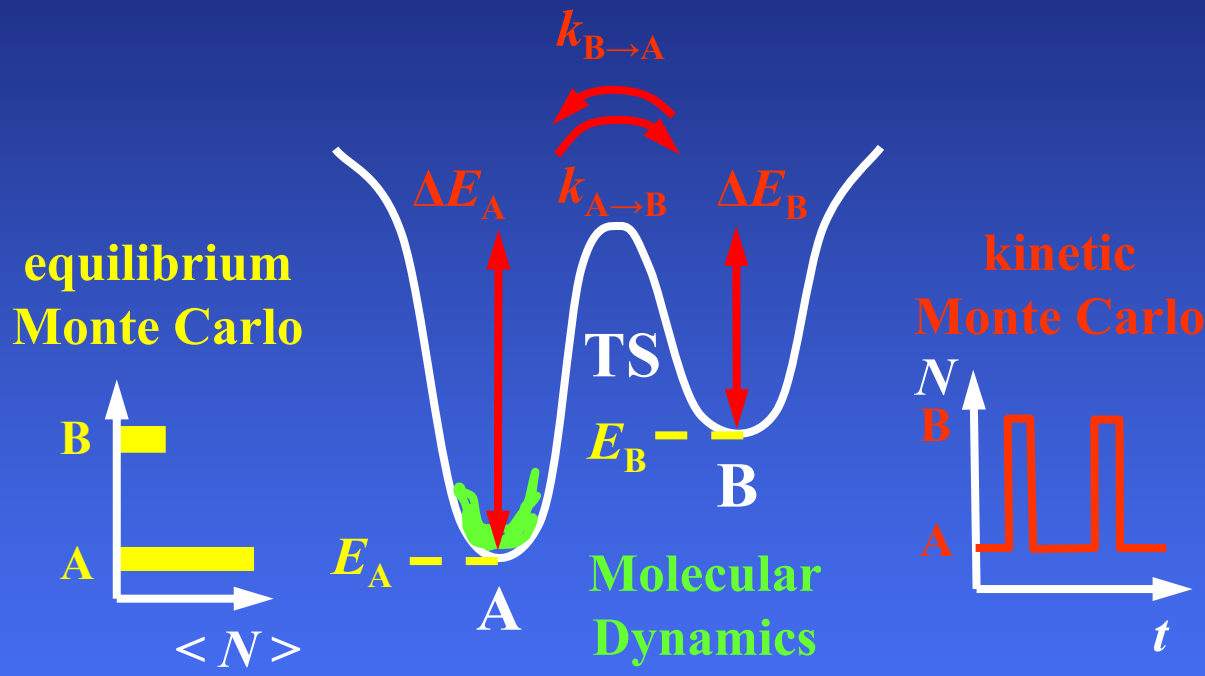


K. Reuter and M. Scheffler,
Phys. Rev. Lett. 90, 046103 (2003)

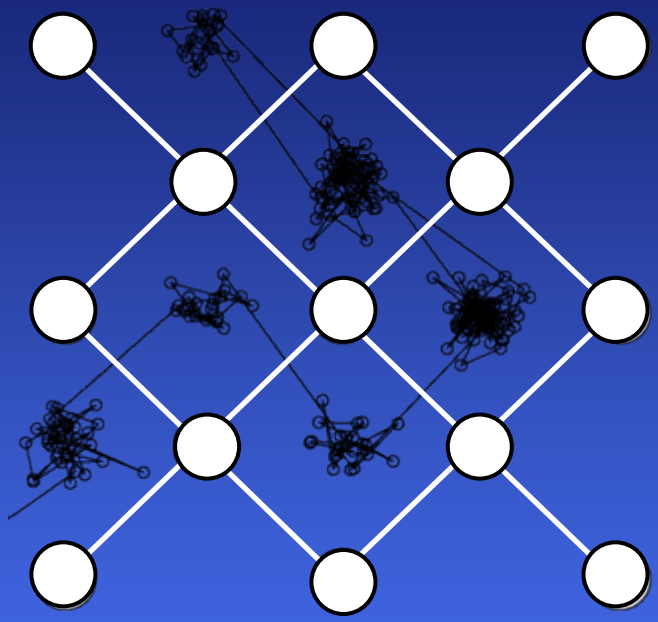
4. Real Kinetics: First-Principles kinetic Monte Carlo Simulations

Ab initio atomistic thermodynamics and statistical mechanics of surface properties and functions
K. Reuter, C. Stampfl and M. Scheffler, in: Handbook of Materials Modeling Vol. 1,
(Ed.) S. Yip, Springer (Berlin, 2005). http://www.fhi-berlin.mpg.de/th/paper.html

First-Principles Kinetic Monte Carlo Simulations

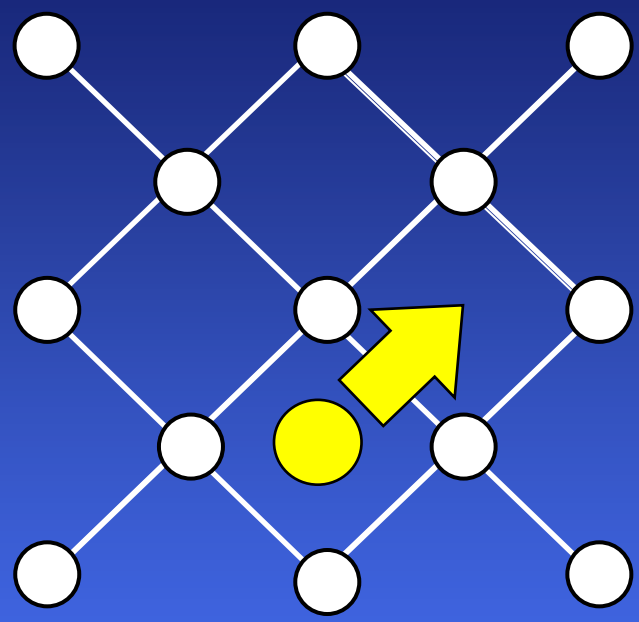


Kinetic Monte Carlo: Essentially Coarse-Grained MD



Molecular Dynamics:
the whole trajectory

ab initio MD:
up to 50 ps

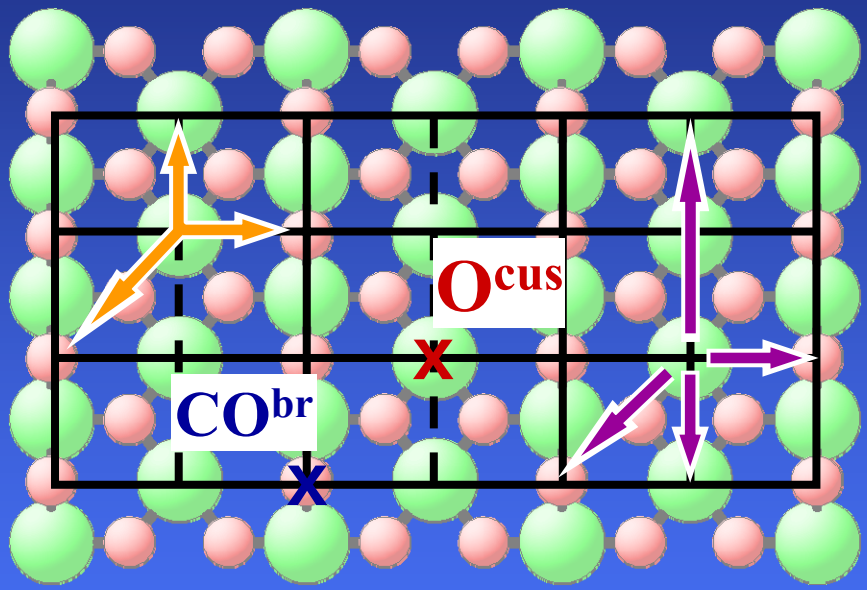


Kinetic Monte Carlo:
coarse-grained hops

ab initio kMC:
up to minutes

The crucial ingredients to a kMC simulation

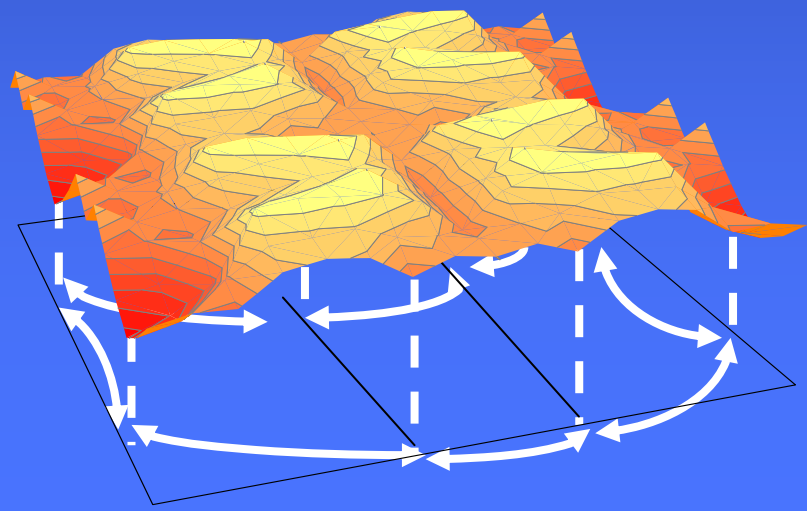
$$\frac{dP(\vec{r},t)}{dt} = -\sum_{\vec{r}'} k(\vec{r} \rightarrow \vec{r}')P(\vec{r},t) + \sum_{\vec{r}'} k(\vec{r}' \rightarrow \vec{r})P(\vec{r}',t)$$



i) Elementary processes

Fixed process list vs. „on-the-fly“ kMC

Lattice vs. off-lattice kMC



ii) Process rates

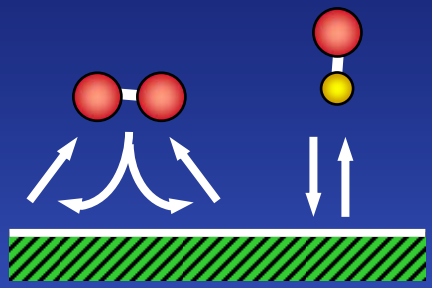
PES from DFT

Transition state theory

$k = k_B T/h \; Z_{TS}/Z_{IS}$

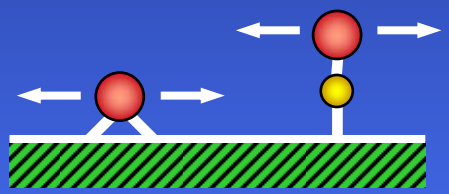
$= \Gamma_0 \exp(-\Delta E/kT)$

kMC Events for CO Oxidation over $RuO_2(110)$

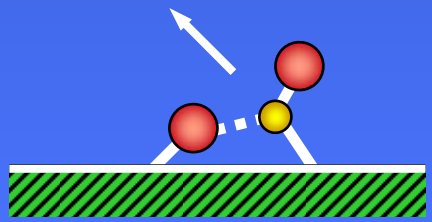


Adsorption: CO - unimolecular, O_2 – dissociative
no barrier
rate given by impingement $k \sim S_o p/(2\pi mkT)$

Desorption: CO – 1st order, O_2 – 2nd order
out of DFT adsorption well (= barrier)
prefactor from detailed balance



Diffusion: hops to nearest neighbor sites
site and element specific
barrier from DFT (TST)
prefactor from DFT (hTST)

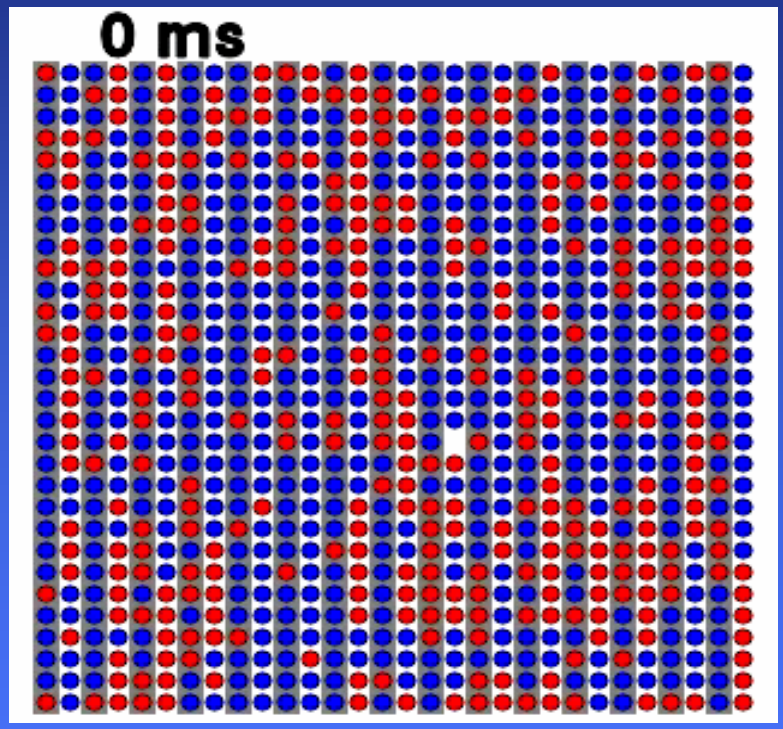


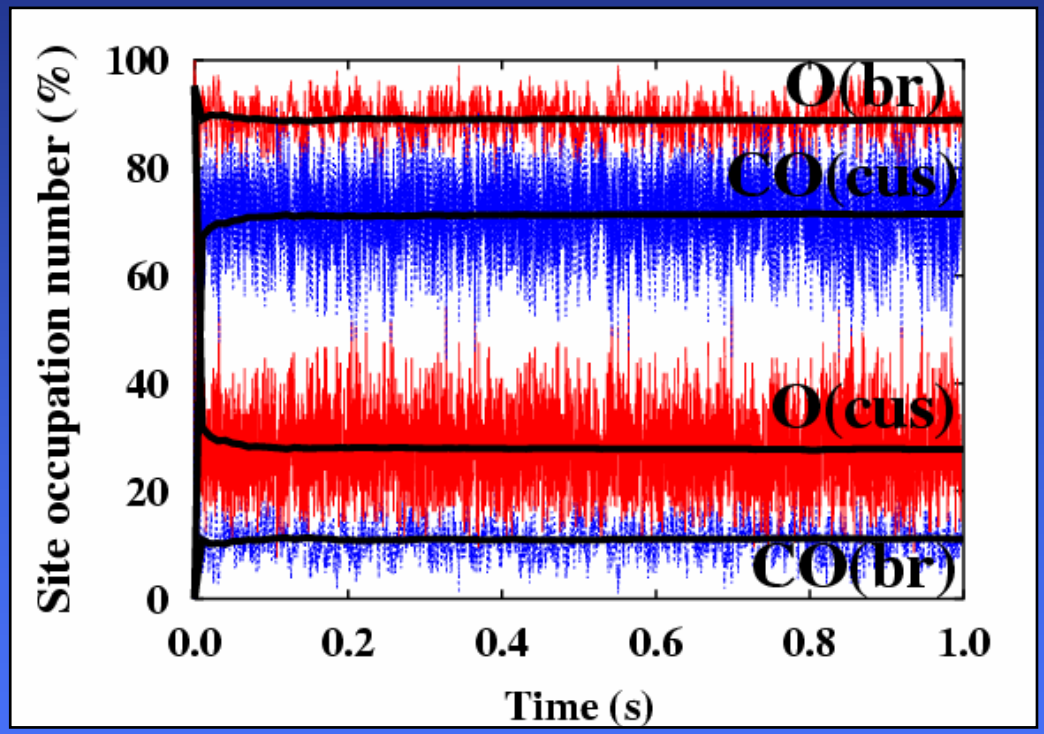
Reaction: site specific
immediate desorption, no readsorption
barrier from DFT (TST)
prefactor from detailed balance

26 elementary processes considered

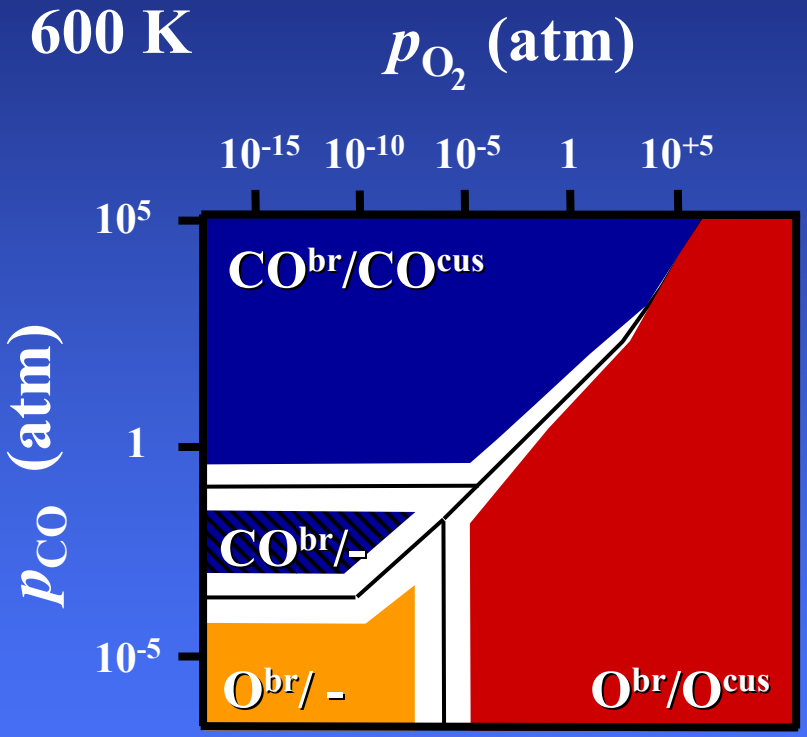
The Steady-State of Heterogeneous Catalysis

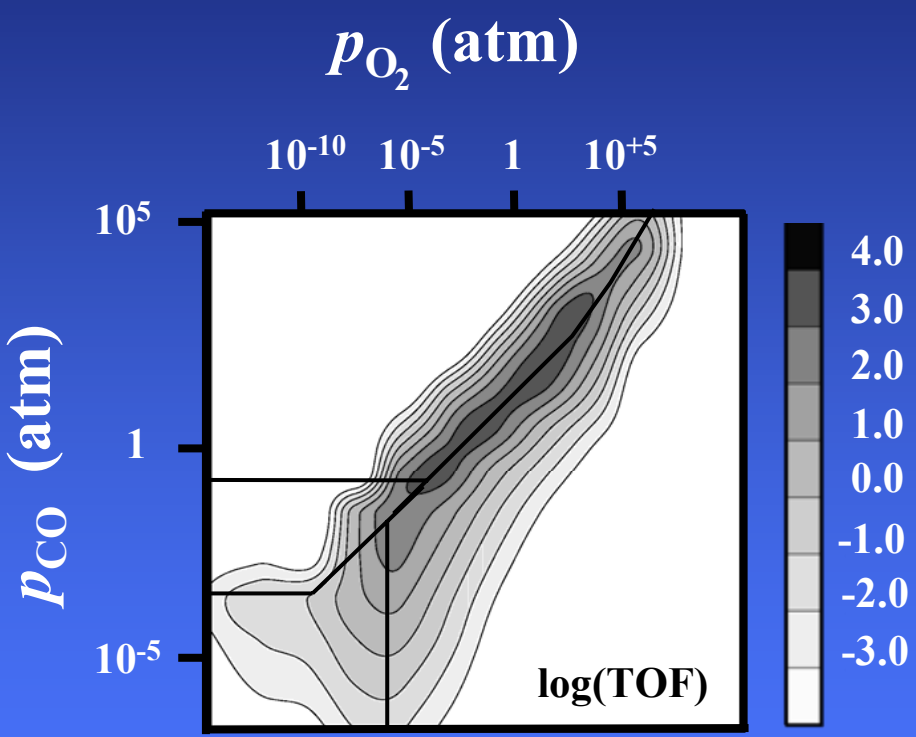
$T = 600$ K $\quad p_{O_2} = 1$ atm $\quad p_{CO} = 7$ atm





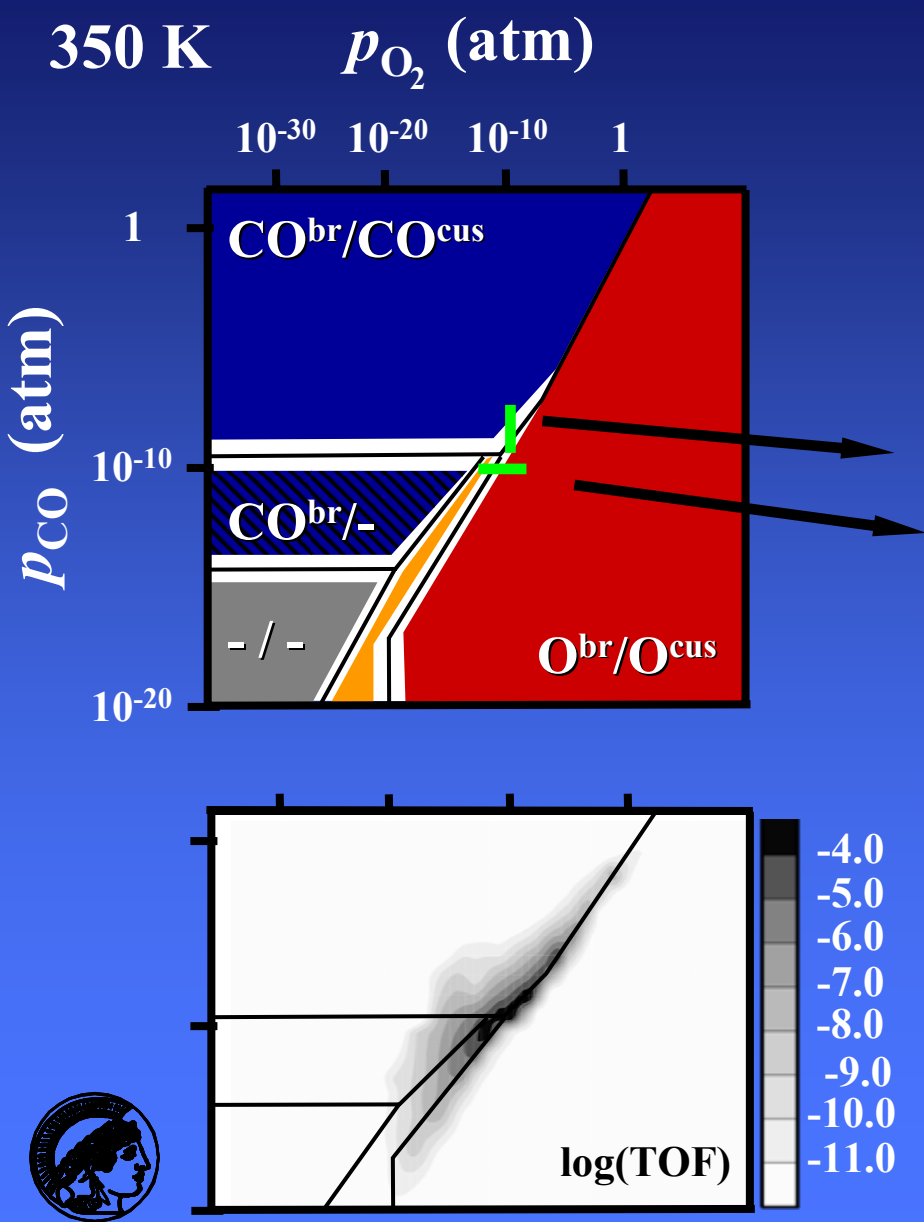
A (p_{CO} , p_{O_2})-Map of Catalytic Activity

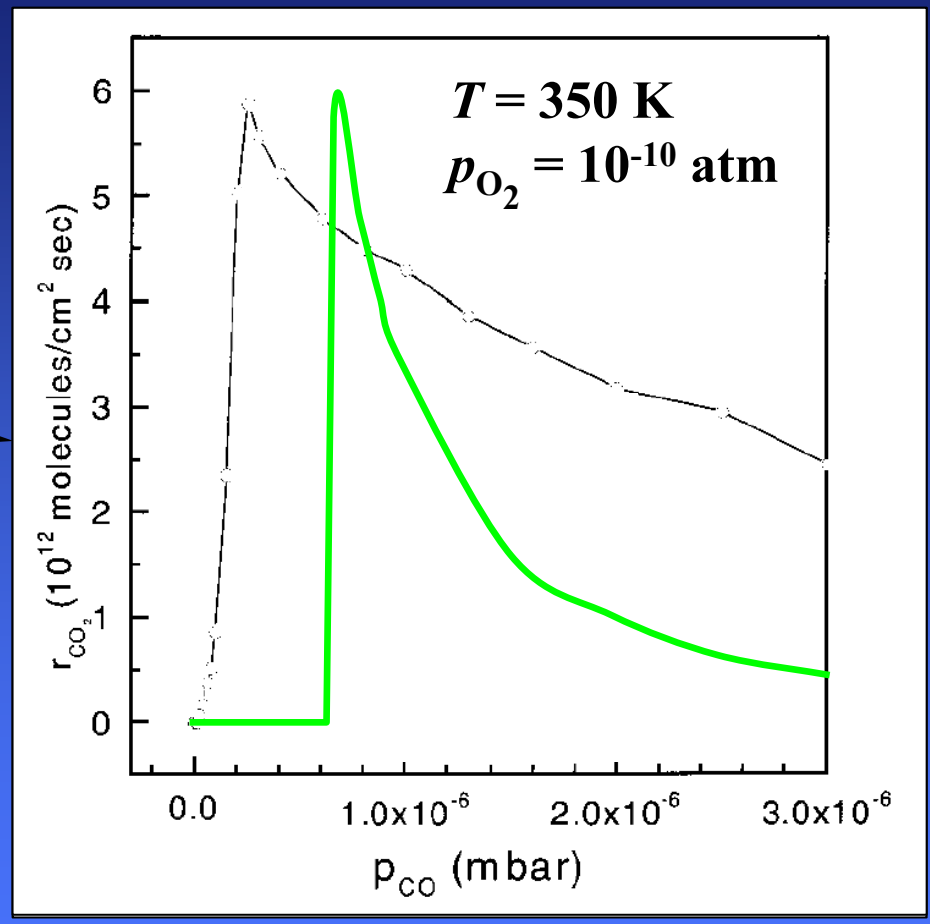




K. Reuter, D. Frenkel and M. Scheffler, Phys. Rev. Lett. 93, 116105 (2004)

…and How About Experiment?



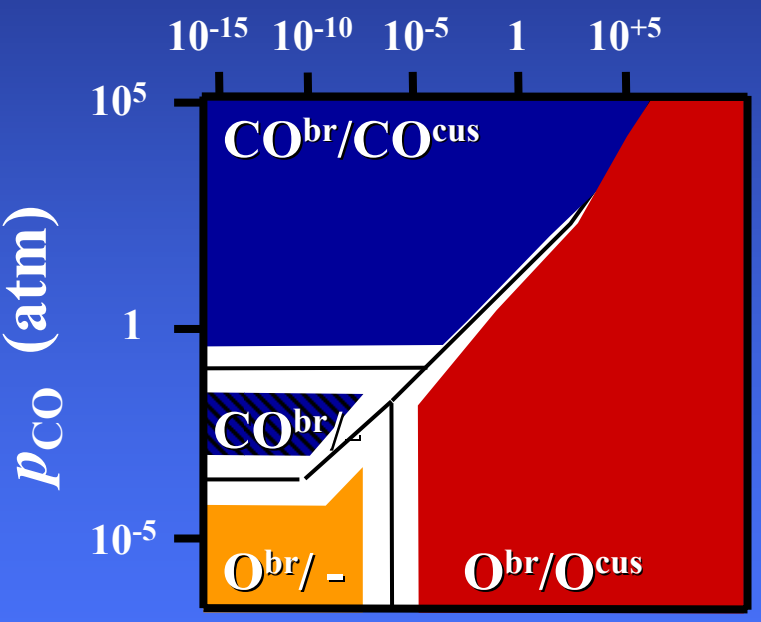


J. Wang *et al.*, J. Phys. Chem. B 106, 3422 (2002)

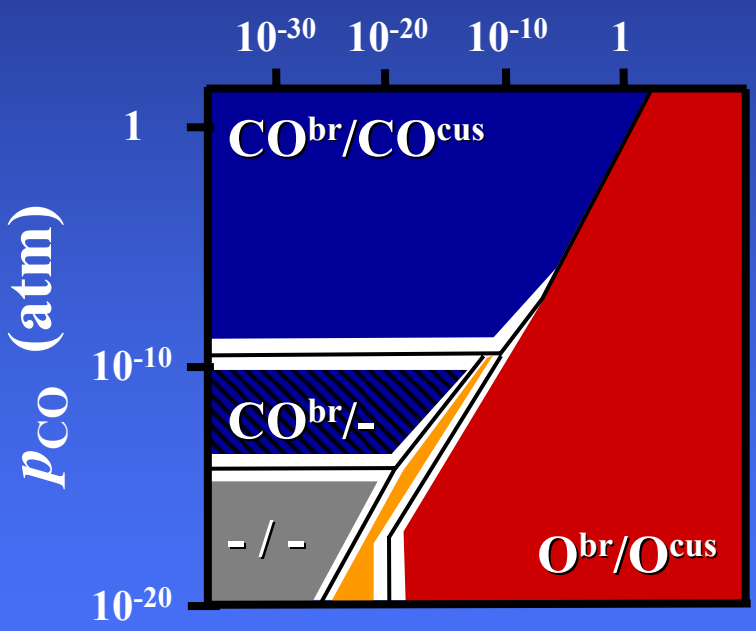
→ cf. NH_3/Ru(0001):
K. Honkala *et al.*, Science 307, 555 (2005)

Thermodynamic Scaling?

600 K



350 K



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

Bridging the Gaps

Still in its infancy… (experimentally and theoretically)

Theory: **First-Principles Statistical Mechanics Approaches**

First-principles atomistic thermodynamics

First-principles kinetic Monte Carlo

Knowledge of surface structure under stationary-reaction conditions

Parameter-free calculation of turnover frequencies (in benign cases)

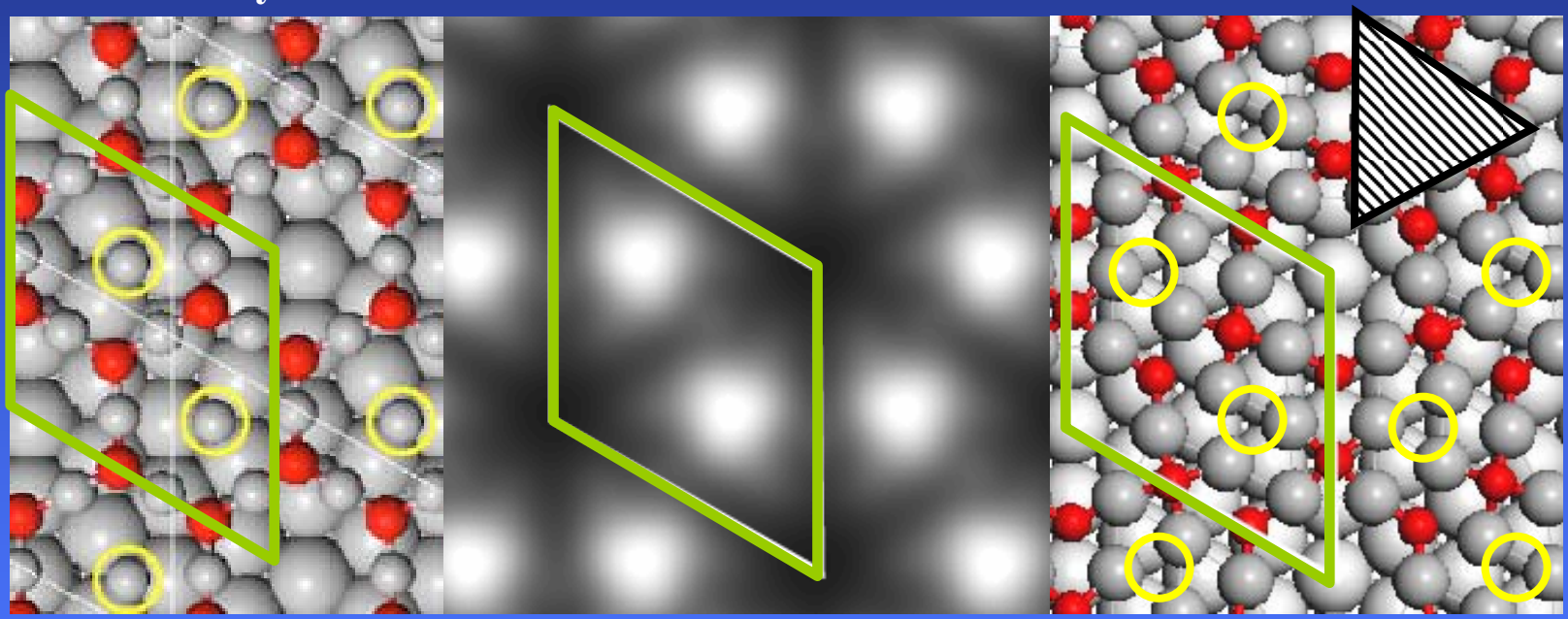
5. Current challenges

Complex structure determination: Ethylene epoxidation at Ag(111)

$Ag_2O(111)$-like overlayer

p(4x4)O / Ag(111)

Ag_6-triangular reconstruction



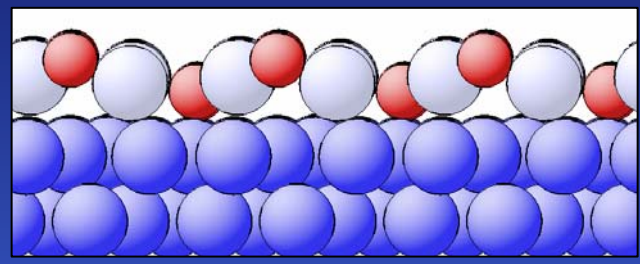
A. Michaelides, K. Reuter, and M. Scheffler, JVST A 23, 1487 (2005)

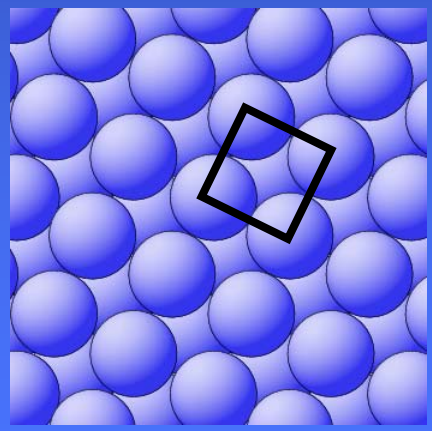
C.I. Carlisle *et al.*, Phys. Rev. Lett. 84, 3899 (2000)

J. Schnadt *et al.*, Phys. Rev. Lett. 96, 146101 (2006); M. Schmid *et al.*, ibid. 96, 146102 (2006)

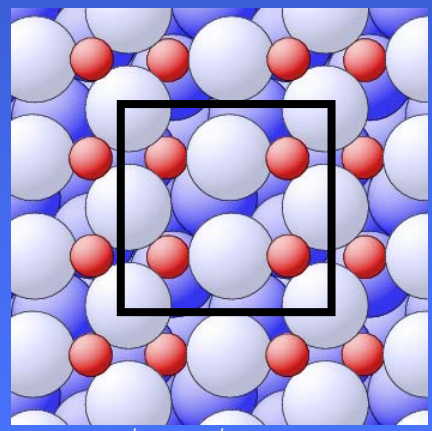
Lattice mapping: CO oxidation at Pd(100)

Catalytically active conditions likely to include continuous formation and reduction of surface oxide structure





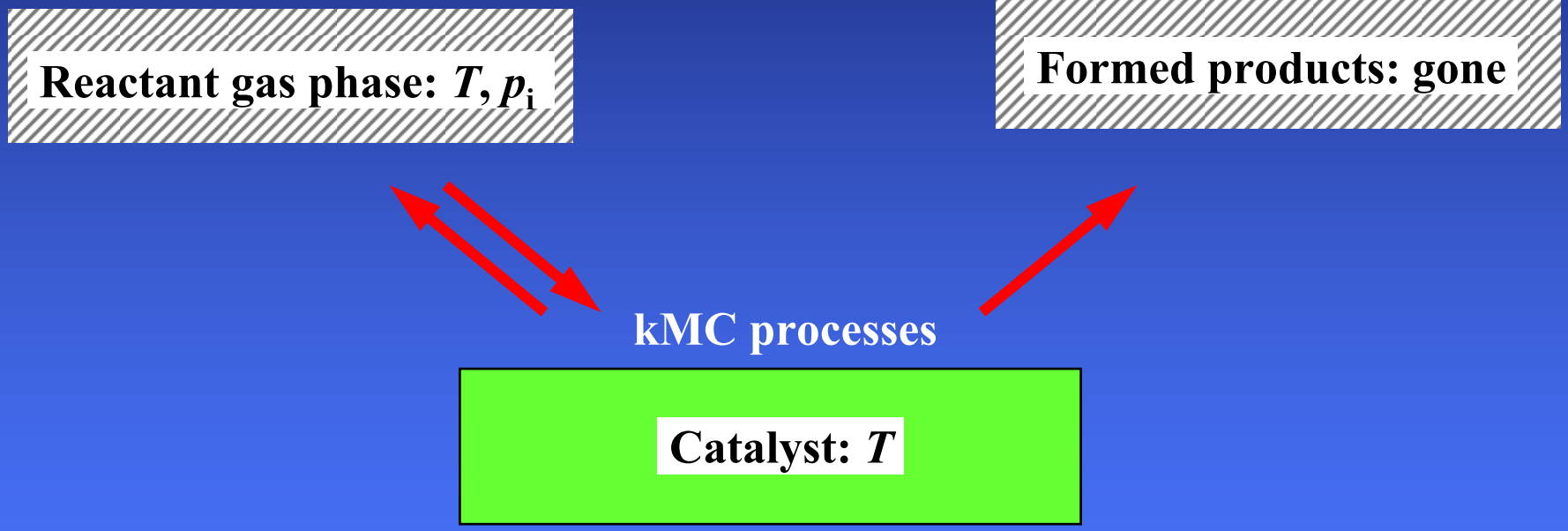
(1 x 1)
Pd(100)



($\sqrt{5}$ x $\sqrt{5}$)*R*27°
PdO(101)/Pd(100)

Lattice mapping of a structural phase transition ?!

Gas phase transport and heat dissipation



Last, not least…

A vacuum is a hell of a lot better than some of the stuff that nature replaces it with.

Tennessee Williams