Ringvorlesung „Modern Methods in Heterogeneous Catalysis“, 19.11.2004

Ab initio atomistic thermodynamics and statistical mechanics of surface properties and functions

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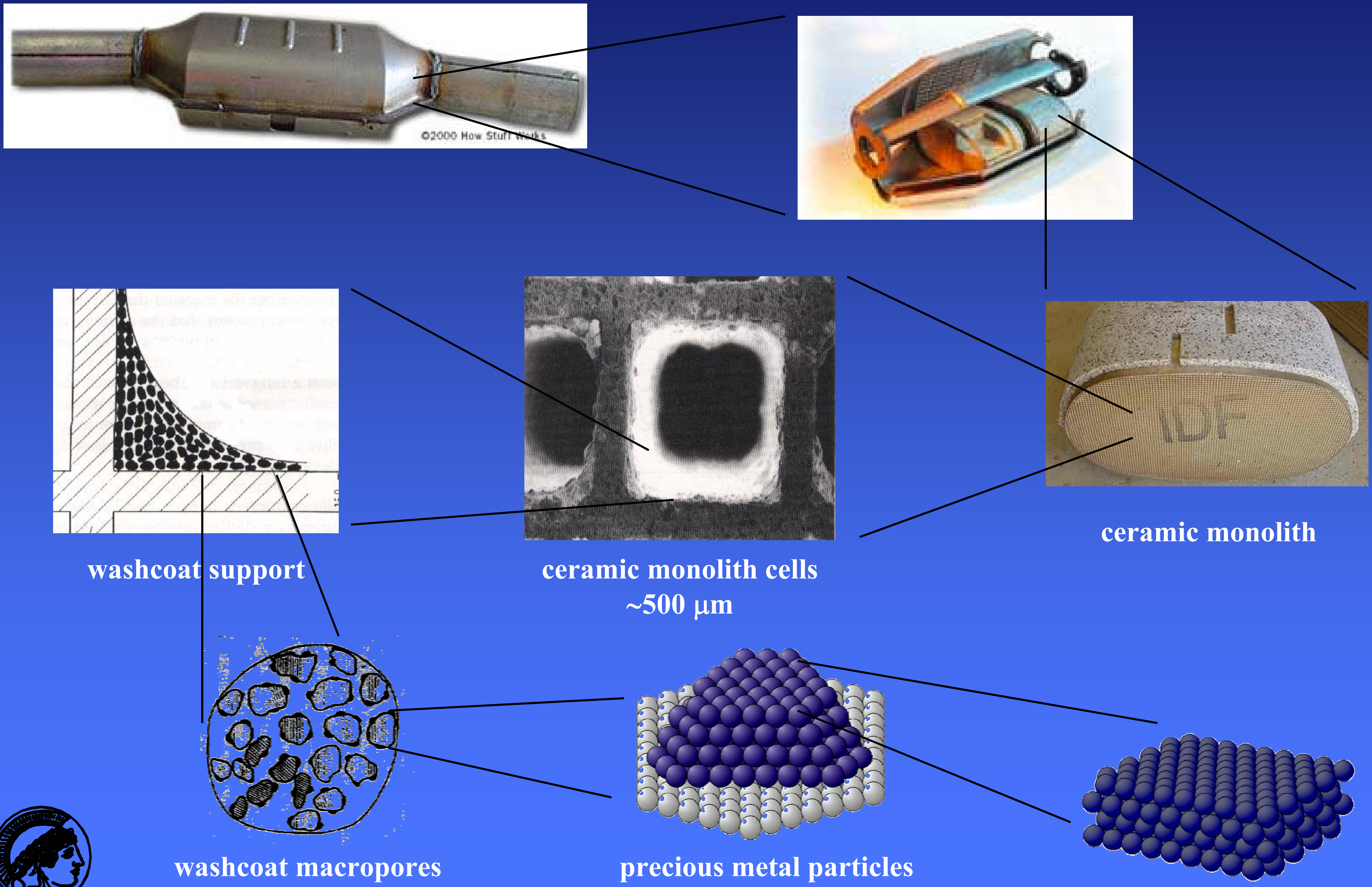
Catalysis: a playground on many levels



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ceramic monolith

washcoat support

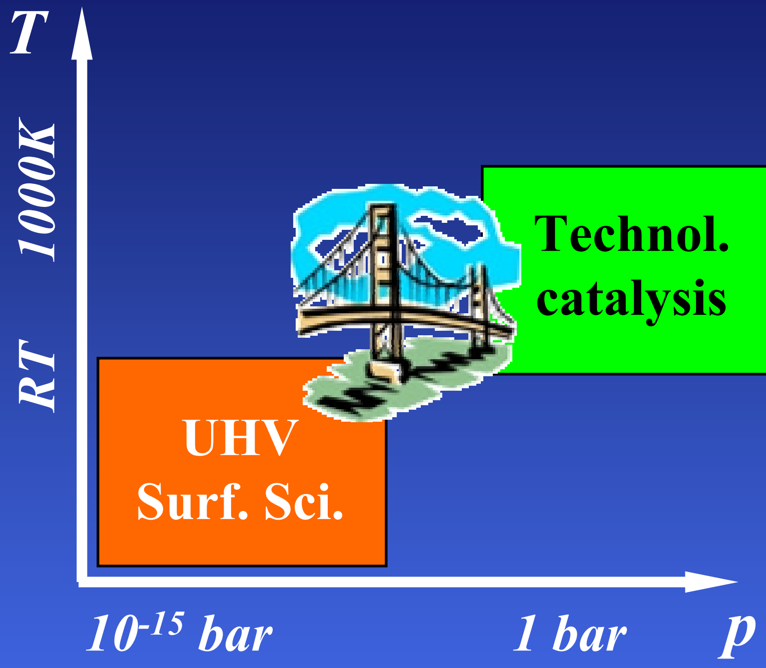
ceramic monolith cells
~500 µm

washcoat macropores
~1-10 µm

precious metal particles
~10-100 nm

single crystal surface

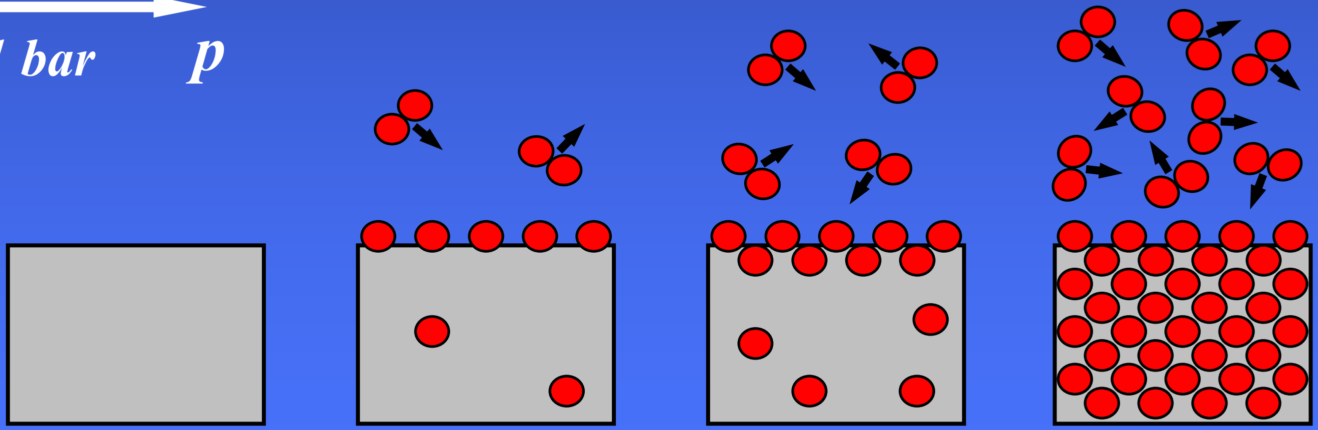
Pressure / materials gap in oxidation catalysis



Low vs. high temperatures

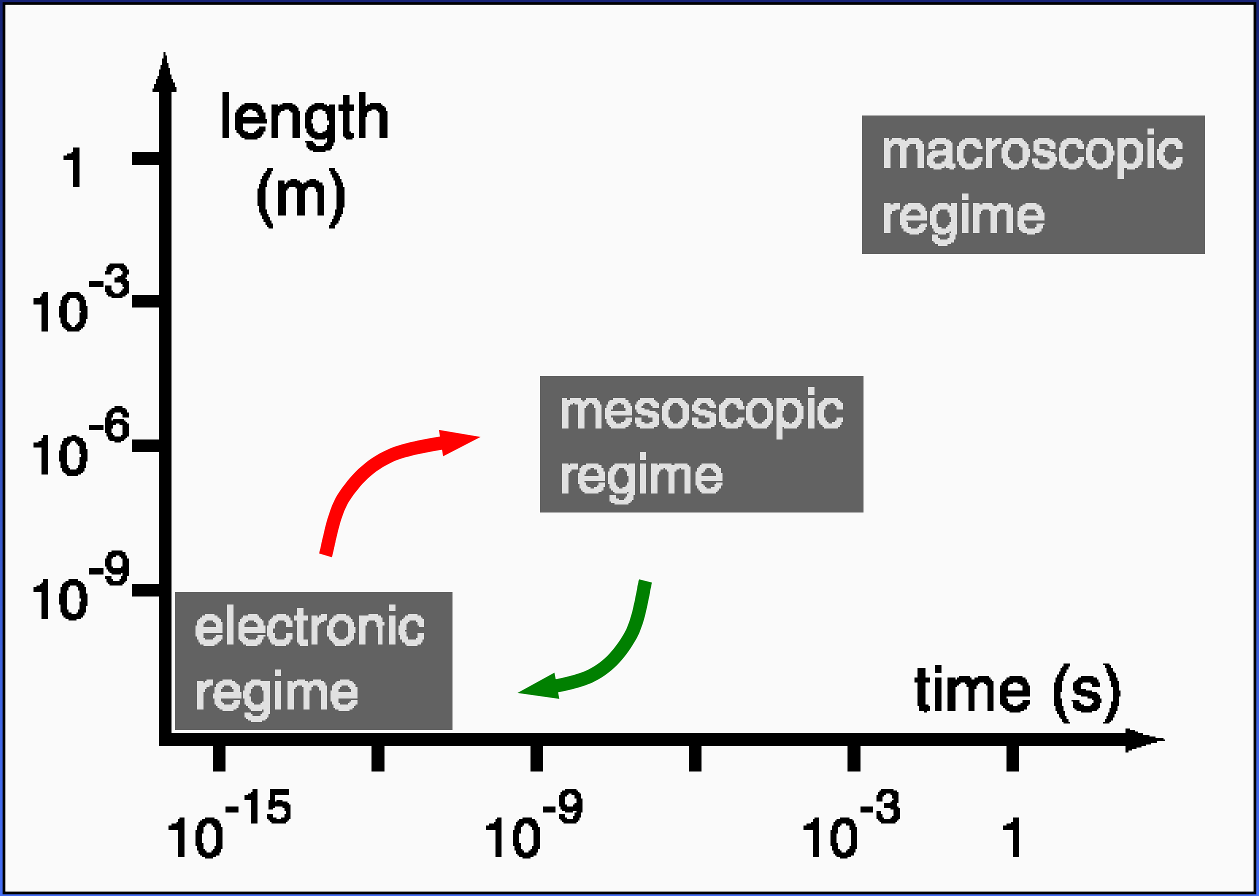
Finite dosage vs.
gas phase reservoir

⇒ oxide formation at the catalyst surface ?!



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 (in press)
http://www.fhi-berlin.mpg.de/th/paper.html

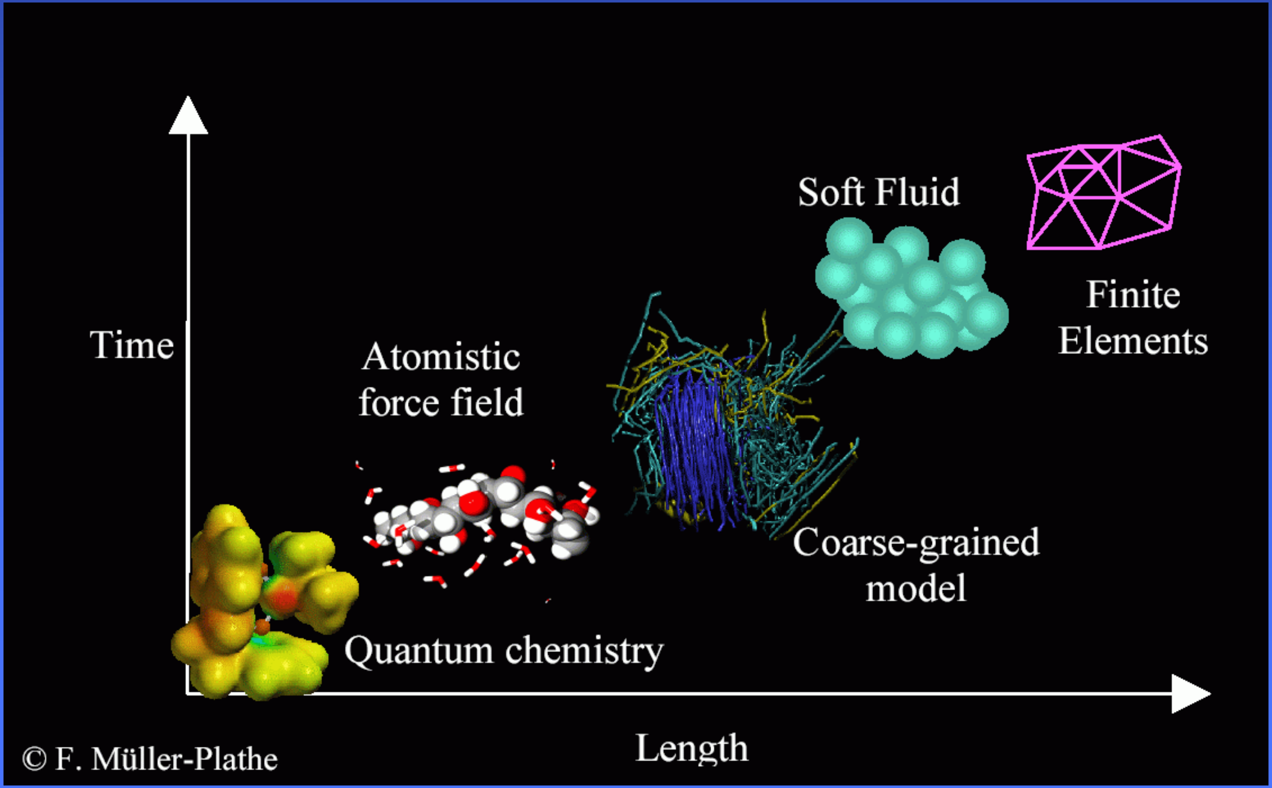
Multiscale modeling



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.) Sidney Yip, Kluwer (in press).
http://www.fhi-berlin.mpg.de/th/paper.html

Coarse graining

e.g.	Colloids:	hard spheres
	Bio-systems:	unified atoms, monomers (residues), polymer/fluid models (connectivity and excluded volume)



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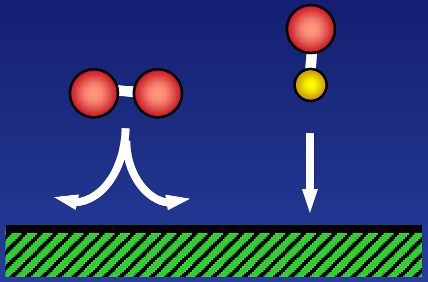
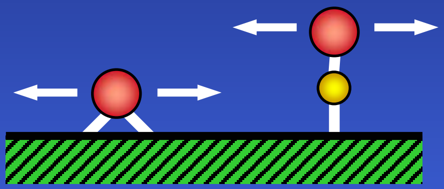
Catalysis:

subtle details of chemical bonding make all the difference

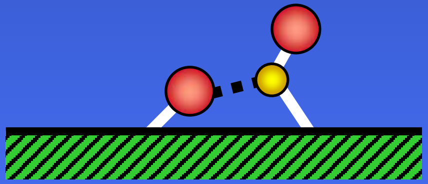
Elementary processes (in heterogeneous catalysis)



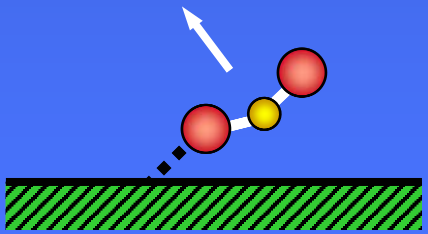
i) (dissociative) adsorption of reactants



ii) diffusion / ordering at the surface



iii) chemical reactions



iv) desorption of reaction products

bond making and breaking:
sometimes fast, but often really really slow

In short:

For a predictive theoretical modeling of heterogeneous catalysis, we need to

- explicitly consider electronic degrees of freedom
  (i.e. electronic structure theory)

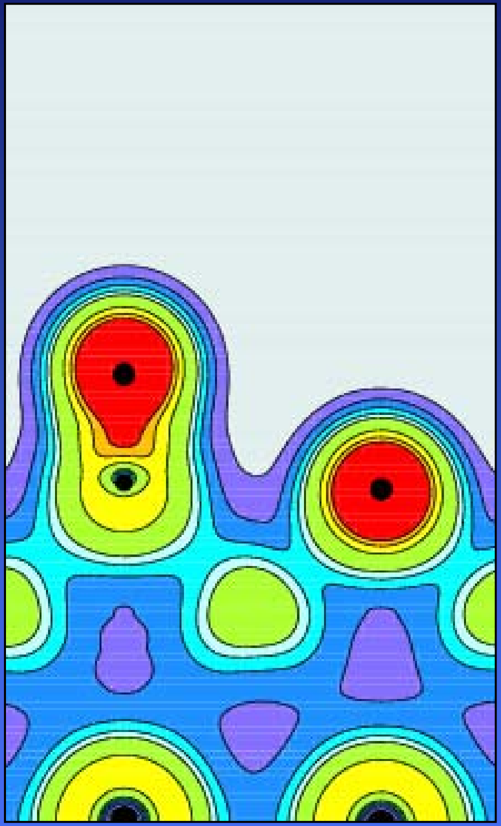
- cover large time scales due to rare event dynamics
  (from phonon period up to ~1 sec)

I. A*b initio* electronic structure calculations of surfaces

***Theoretical Surface Science*,**
A. Groß, Springer (Berlin, 2002)

Electronic structure methods

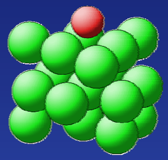
Tight-binding
Density-functional theory
Quantum chemical methods (> HF)
(Quantum Monte Carlo)



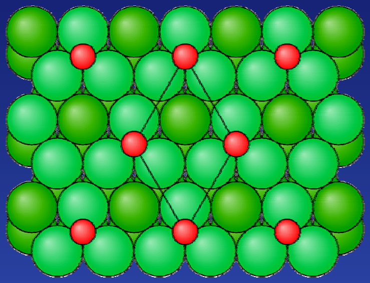
- Total energy
- Forces (relaxation, vibrations, MD…)
- Electronic structure (…)

But: manageable system sizes ~ 1000 electrons (DFT: n^3)
known inaccuracies due to V_{xc}

Surface models: slabs vs. clusters



vs.

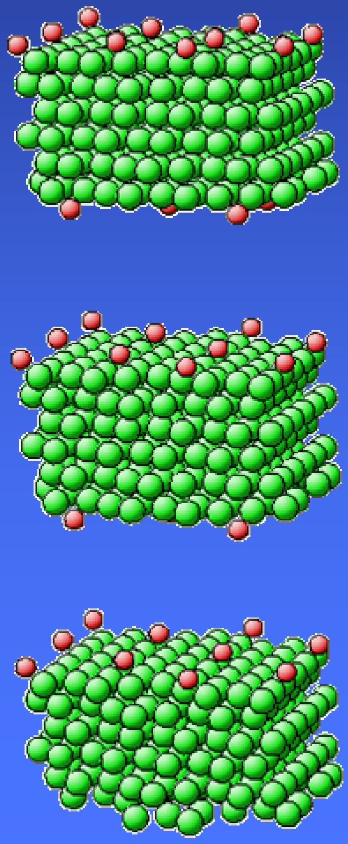


Cluster geometries:

- + very cheap for small clusters (local basis sets)
- + ideal for local aspects (defects etc.)
- – slow convergence with cluster size (embedding etc.)

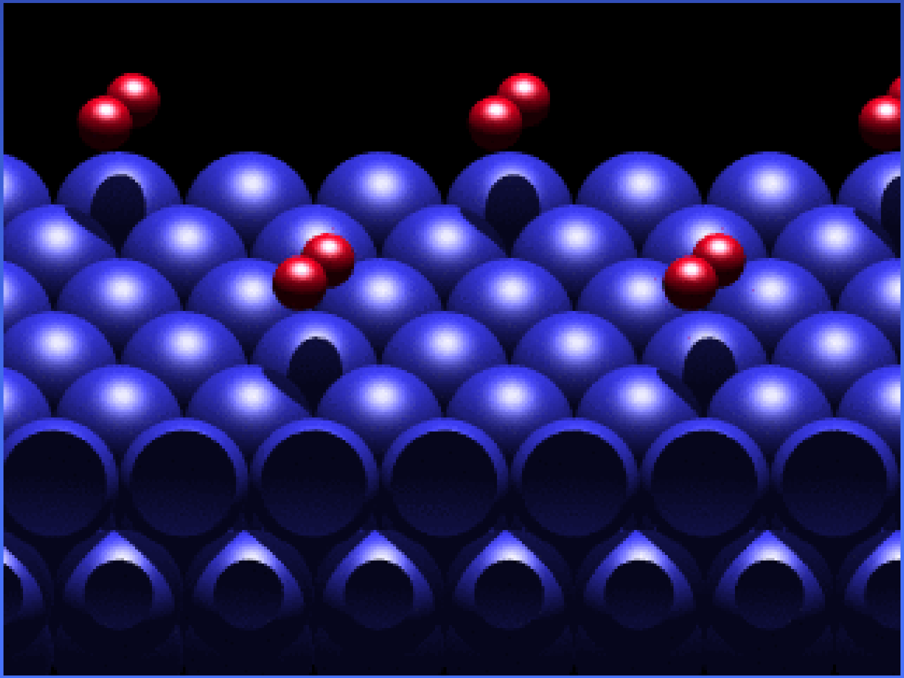
Supercell geometries (“slabs”):

- + proper surface electronic structure (band structure)
- + good convergence with slab thickness (“semi-infinite”)
- + suitable for plane wave basis sets
- – artificial lateral periodicity: “ordered arrays”
- – inherently expensive (large systems)



Keeping everything: *ab initio* molecular dynamics

MD:	follow time evolution explicitly (numerical integration of Newton's equation of motion, $F = m a$)
***Ab initio* MD:**	get forces from first-principles calculations



J. Behler *et al.*, Phys. Rev. Lett. (submitted)

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

In short:

With explicit *ab initio* MD we can presently

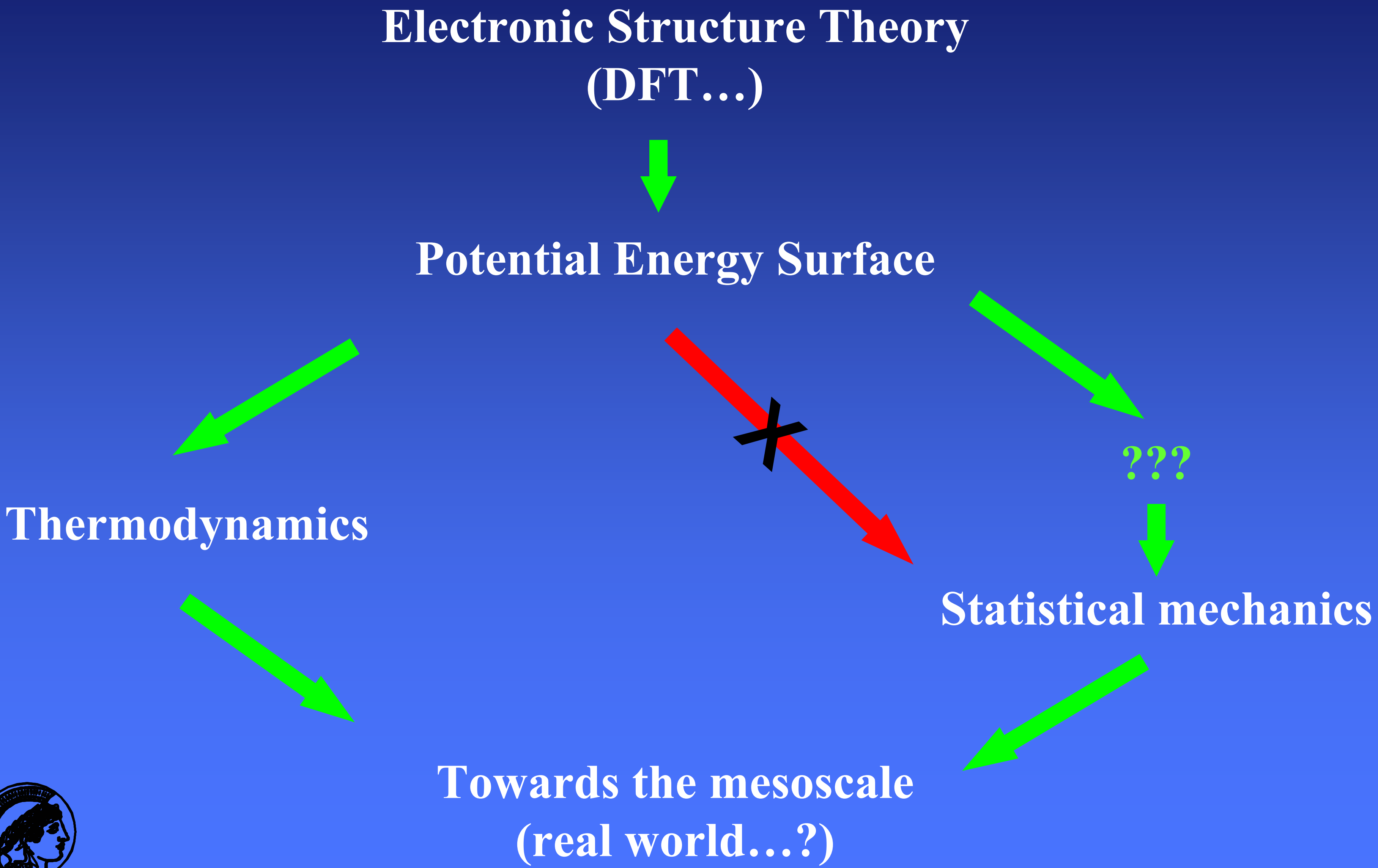
- treat only very limited system sizes (periodic supercells)
- get at best up to about 50 ps, which is ~10 orders of magnitude short of where we want to go…

Option A: give up, do bio, get money and fame…

Option B: find more efficient ways of modeling
(e.g. by suitable coarse graining)

„First-principles statistical mechanics“

From micro to meso



Electronic Structure Theory
(DFT…)

Potential Energy Surface

Thermodynamics

???

Statistical mechanics

Towards the mesoscale
(real world…?)

II. *Ab initio* atomistic thermodynamics

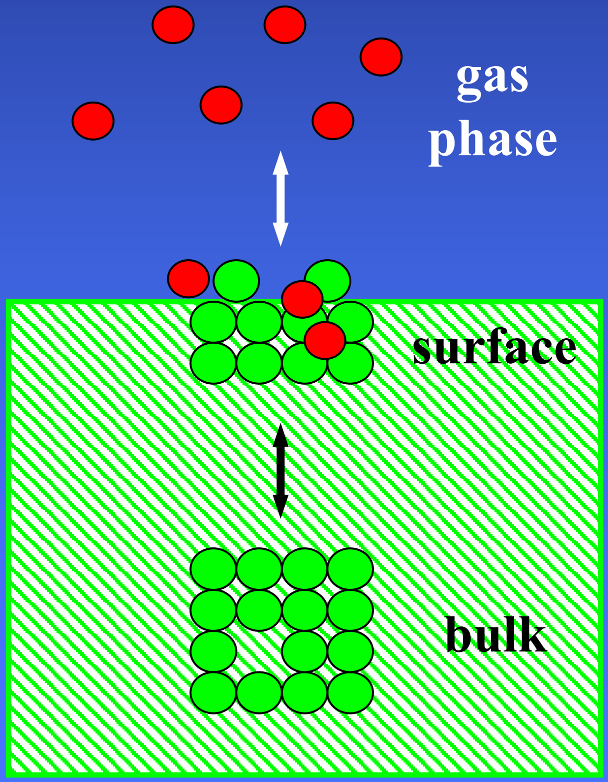
Statistical Mechanics,
D.A. McQuarrie, Harper Collins Publ. (1976)

Introduction to Modern Statistical Mechanics,
D. Chandler, Oxford Univ. Press (1987)

General idea

Extend the length scale by

- separating system into sub-systems (reservoirs!)
- calculate properties of sub-systems separately
- connect by implying equilibrium between sub-systems



Drawback:

- no temporal information
  („system properties after infinite time“)
- equilibrium assumption

Thermodynamics in a nutshell

Internal energy (U)	$E^{tot}(S,V)$
Enthalpy	$H(S,p) = E^{tot} + pV$
(Helmholtz) free energy	$F(T,V) = E^{tot} - TS$
Gibbs free energy	$G(T,p) = E^{tot} - TS + pV$

Potential functions

- **Equilibrium state of system minimizes corresponding potential function**

- **In its set of variables the total derivative of each potential function is simple (derive from 1st law of ThD:** $dE^{tot} = dQ + dW$, $dW = -pdV$, $dQ = TdS$**)**

$$dE = TdS - pdV$$
$$dH = TdS + Vdp$$
$$dF = -SdT - pdV$$
$$dG = -SdT + Vdp$$

$\Rightarrow$ **These expressions open the gate to a whole set of general relations like:**

$$S = -(\partial F/\partial T)_V\,,\ p = -(\partial F/\partial V)_T$$

$$E^{tot} = -T^2\,(\partial/\partial T)_V\,(F/T)$$ **Gibbs-Helmholtz eq.**

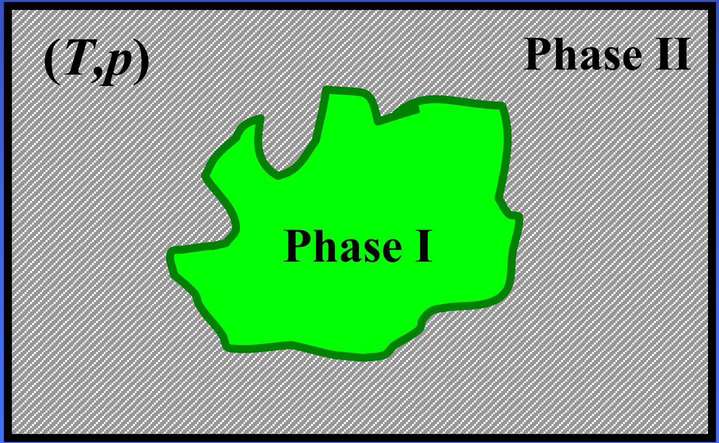
$$(\partial T/\partial V)_S = -(\partial p/\partial S)_V$$ **etc. Maxwell relations**

- **Chemical potential** $\mu = (\partial G/\partial n)_{T,p}$ **is the cost to remove a particle from the system.**
  Homogeneous system: $\mu = G/N\ (= g)$
  i.e. Gibbs free energy per particle

Surface thermodynamics

A surface can never be alone:
there are always
"two sides" to it !!!

solid – gas
solid – liquid
solid – solid ("interface")
…



Phase I / phase II alone (bulk):

$$G_{\mathrm{I}} = N_{\mathrm{I}}\, \mu_{\mathrm{I}}$$
$$G_{\mathrm{II}} = N_{\mathrm{II}}\, \mu_{\mathrm{II}}$$

Total system (with surface):

$$G_{\mathrm{I+II}} = G_{\mathrm{I}} + G_{\mathrm{II}} + \underbrace{\Delta G_{\mathrm{surf}}}_{\gamma A}$$

$$\boxed{\gamma = 1/A\ \left(G_{\mathrm{I+II}} - \textstyle\sum_{\mathrm{i}} N_{\mathrm{i}}\, \mu_{\mathrm{i}} \right)}$$

Surface tension
(free energy per area)

Computation of free energies: solids

$$\boxed{G(T,p) \; = \; E^{tot} + F^{trans} + F^{rot} + F^{vib} + F^{conf} + pV}$$

F^{trans}	**Translational free energy**	$\propto 1/M \rightarrow 0$
F^{rot}	**Rotational free energy**	
pV	$V = V(T,p)$ **from equation of state, varies little**	$\rightarrow 0$ **for** $p < 100$ **atm**
F^{conf}	**Configurational free energy**	→ **depends on application**
E^{tot}	**Internal energy**	→ **DFT**
F^{vib}	**Vibrational free energy**	→ **phonon band structure**

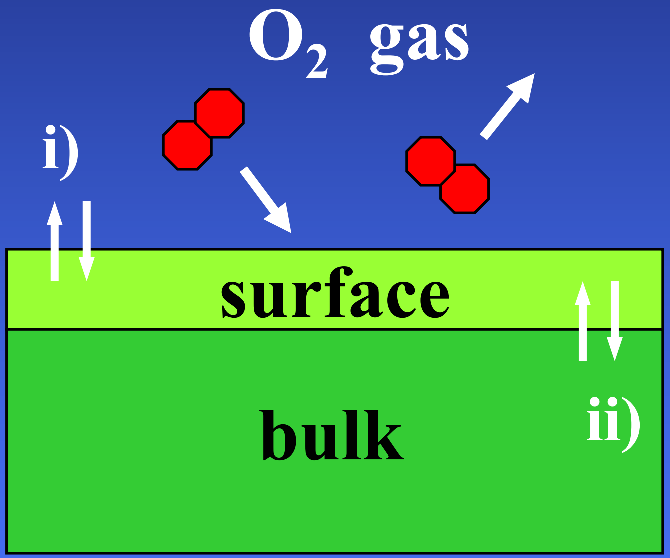
E^{tot}, F^{vib} **use differences**

use simple models to approx. F^{vib} **(Debye, Einstein)**

⇒ **Solids (low T):** $G(T,p) \sim E^{tot} + F^{conf}$

Example: Surface in contact with oxygen gas phase

$$\gamma_{\text{surf.}} = 1/A\,[\,G_{\text{surf.}}(N_{\text{O}}, N_{\text{M}}) - N_{\text{O}}\,\mu_{\text{O}} - N_{\text{M}}\,\mu_{\text{M}}\,]$$



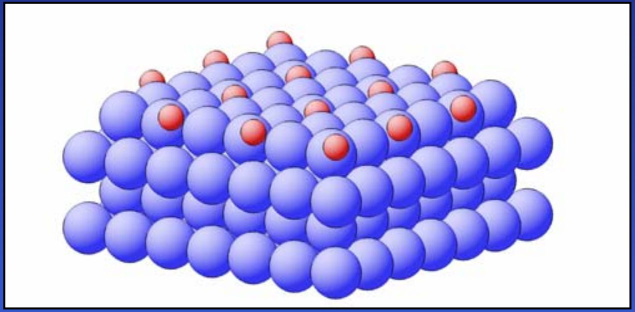
i) μ_{O} from ideal gas

ii) $\mu_{\text{M}} = g_{\text{M}}^{\text{bulk}}$

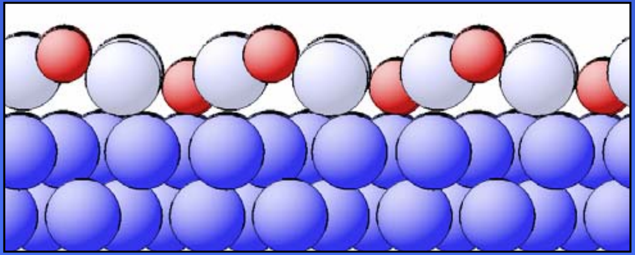
$$\boxed{\gamma(T,p) \approx (\,E^{(\text{slab})}_{\text{surf.}} - N_{\text{M}}\,E^{\text{bulk}}_{\text{M}}\,)/A \;-\; N_{\text{O}}\,\mu_{\text{O}}(T,p)\,/A}$$

Oxide formation on Pd(100)

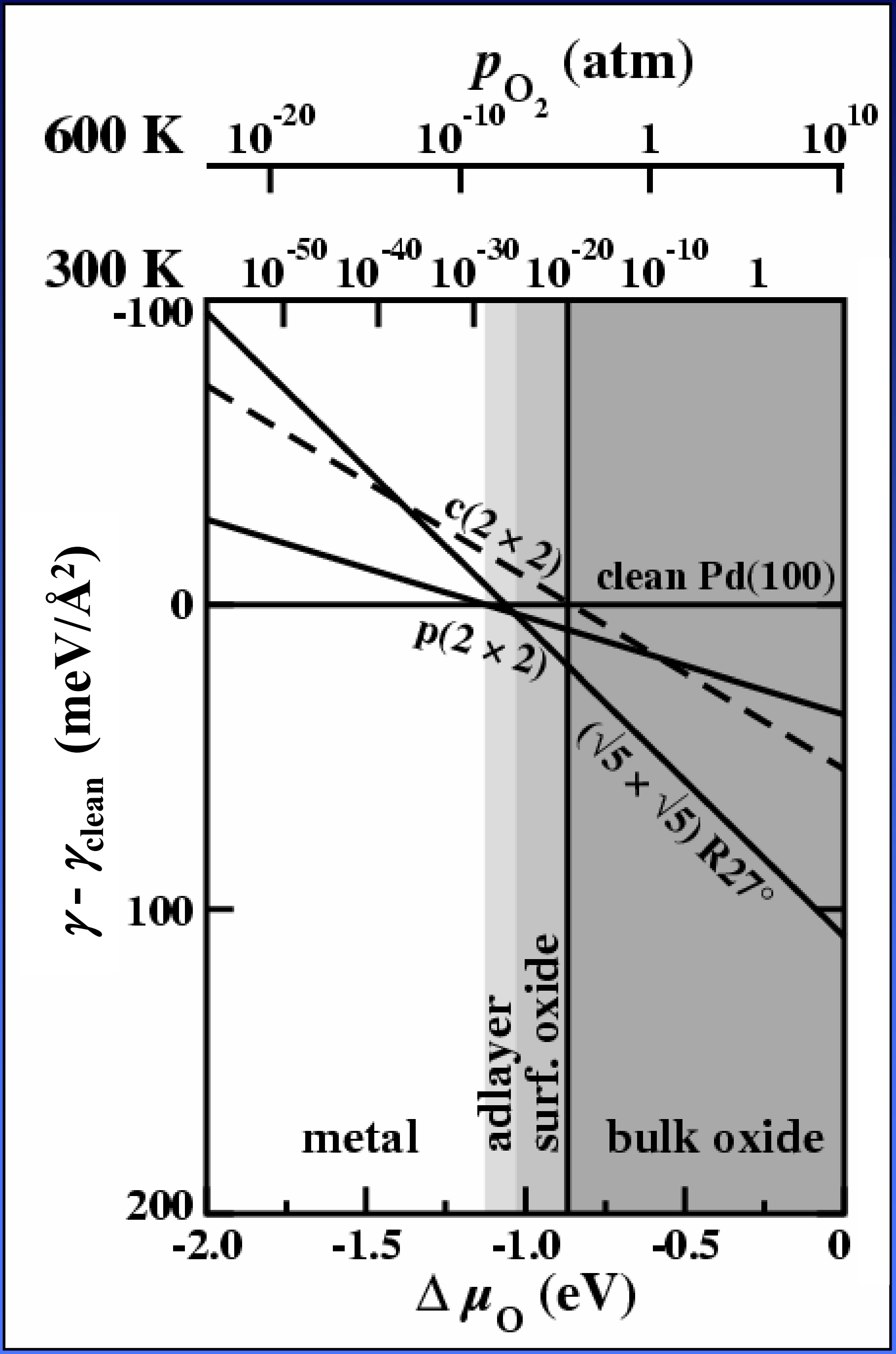
$$\gamma \approx \left(E^{(\mathrm{slab})}_{\mathrm{surf.}} - N_{\mathrm{M}}\, E^{\mathrm{bulk}}_{\mathrm{M}} \right)/A \;-\; N_{\mathrm{O}}\, \mu_{\mathrm{O}}/A$$



p(2x2) O/Pd(100)

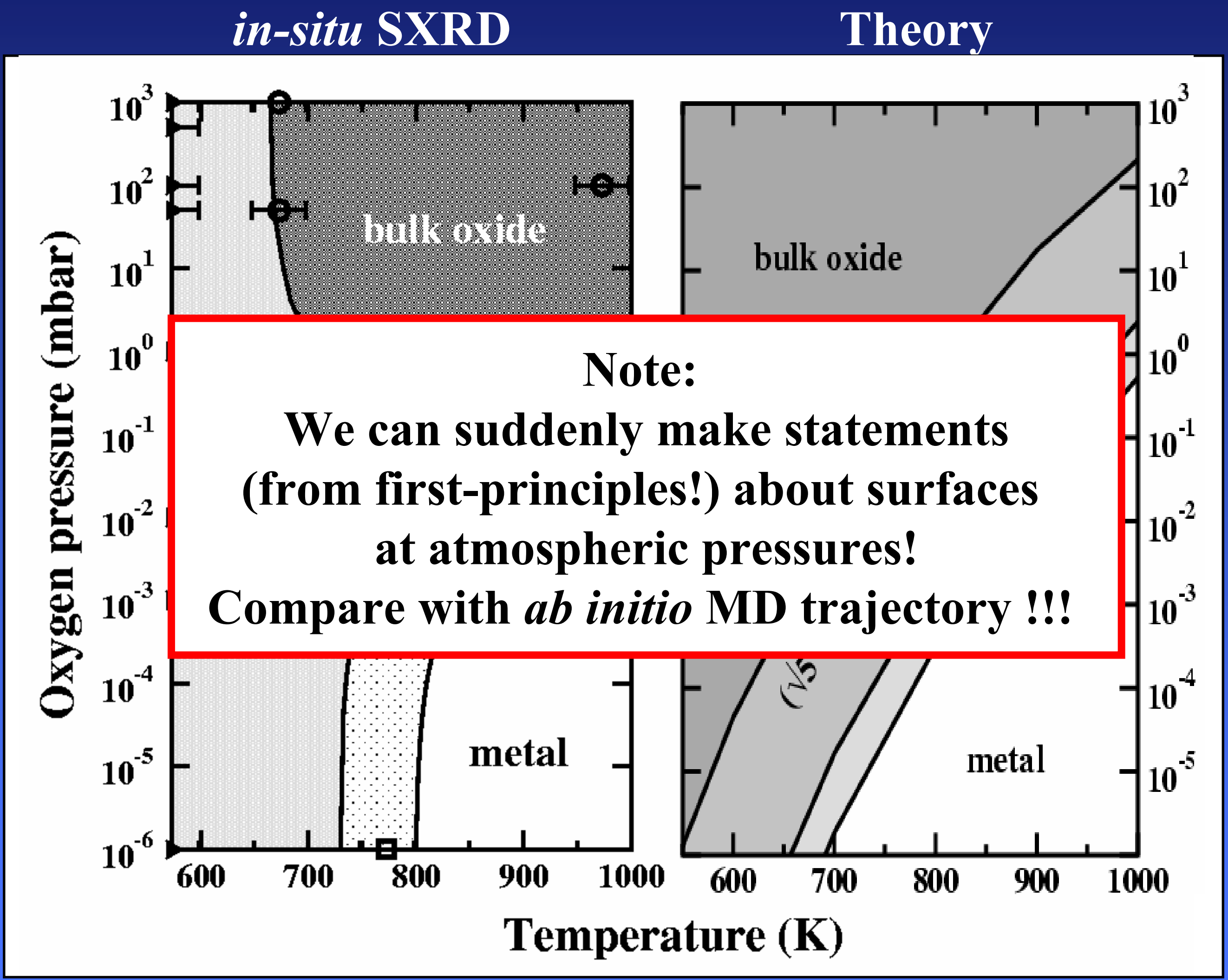


(√5 x √5)R27° PdO(101)/Pd(100)



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

Comparing with experiment: kinetik effects

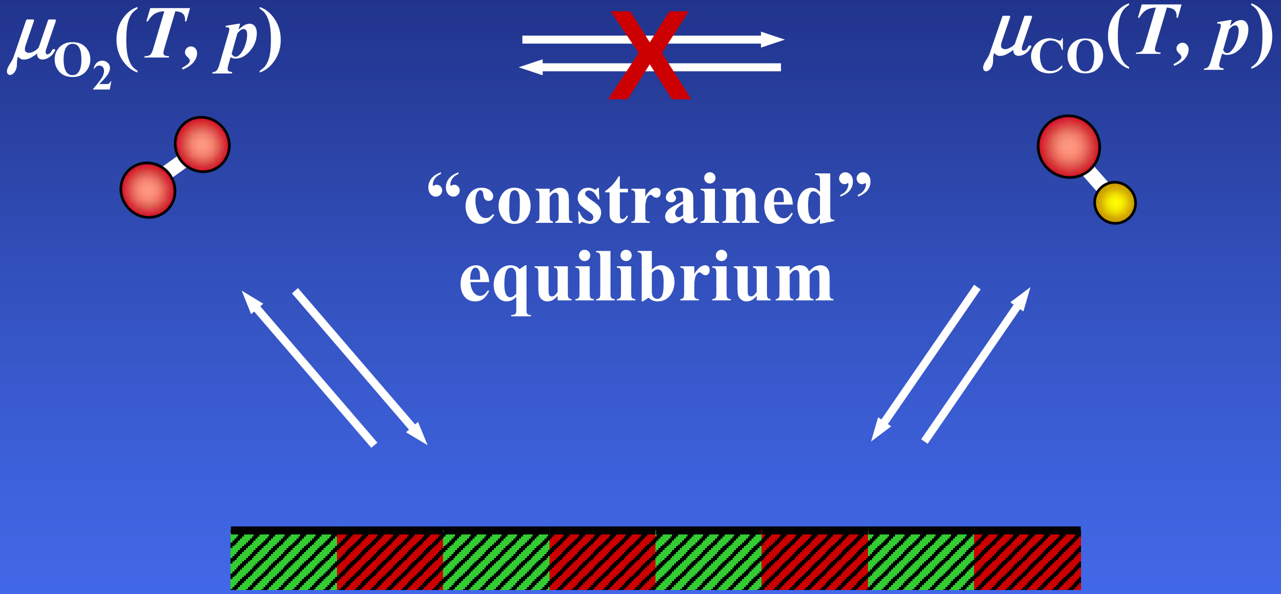


Note:
We can suddenly make statements (from first-principles!) about surfaces at atmospheric pressures!
Compare with *ab initio* MD trajectory !!!

Experiment: E. Lundgren (U Lund)
A. Stierle (MPG Stuttgart)

E. Lundgren *et al.*,
Phys. Rev. Lett. 92, 046101 (2004)

Application to catalysis: reactive multi-component gas phase



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

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

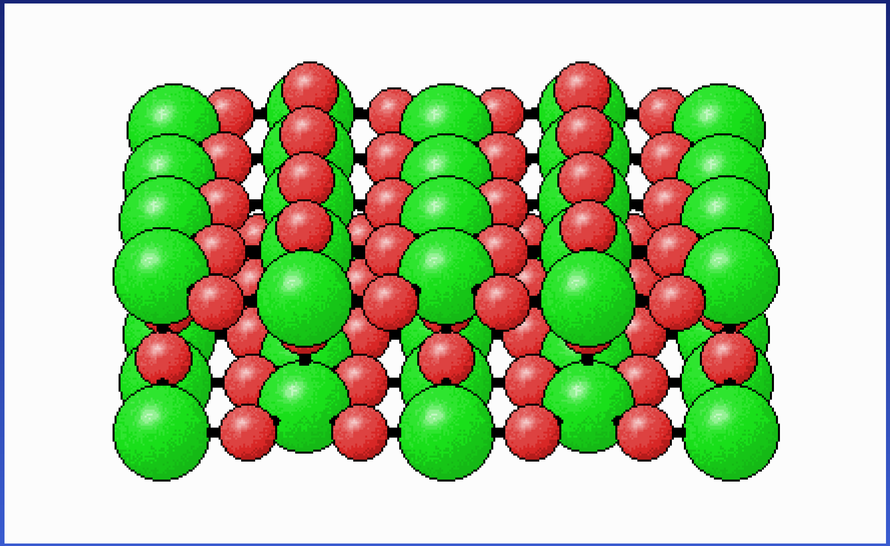
"constrained" equilibrium

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

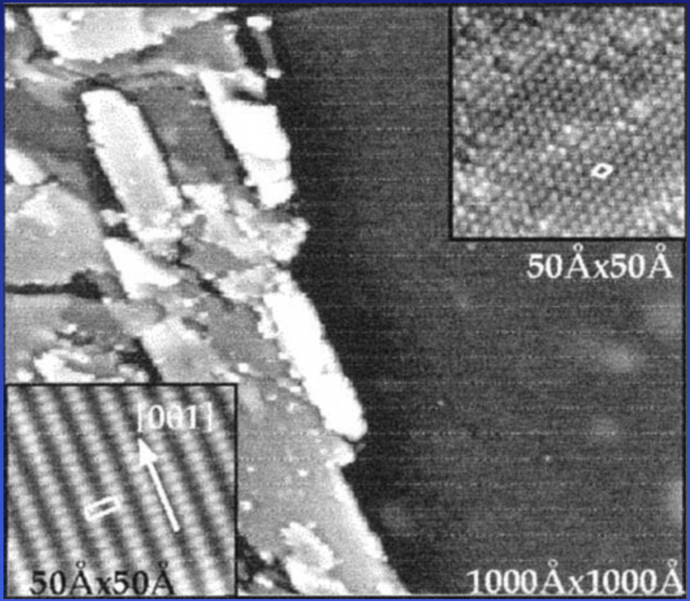
C.M. Weinert and M. Scheffler,
Mater. Sci. Forum 10-12, 25 (1986);
E. Kaxiras *et al.*, Phys. Rev. B 35, 9625 (1987)

K. Reuter and M. Scheffler,
Phys. Rev. B 65, 035406 (2002);
Phys. Rev. B 68, 045407 (2003)

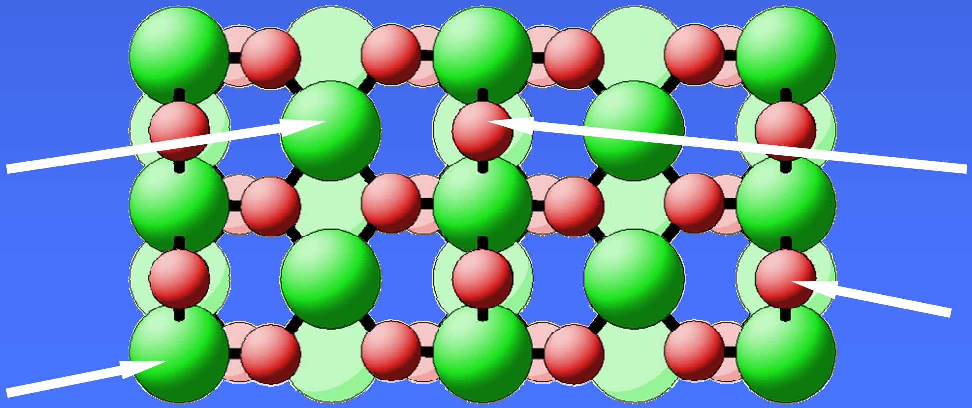
Materials gap: Ru(0001) vs. RuO$_2$(110)



K. Reuter *et al*., Chem. Phys. Lett. 352, 311 (2002)



H. Over and M. Muhler,
Prog. Surf. Sci. 72, 3 (2004)



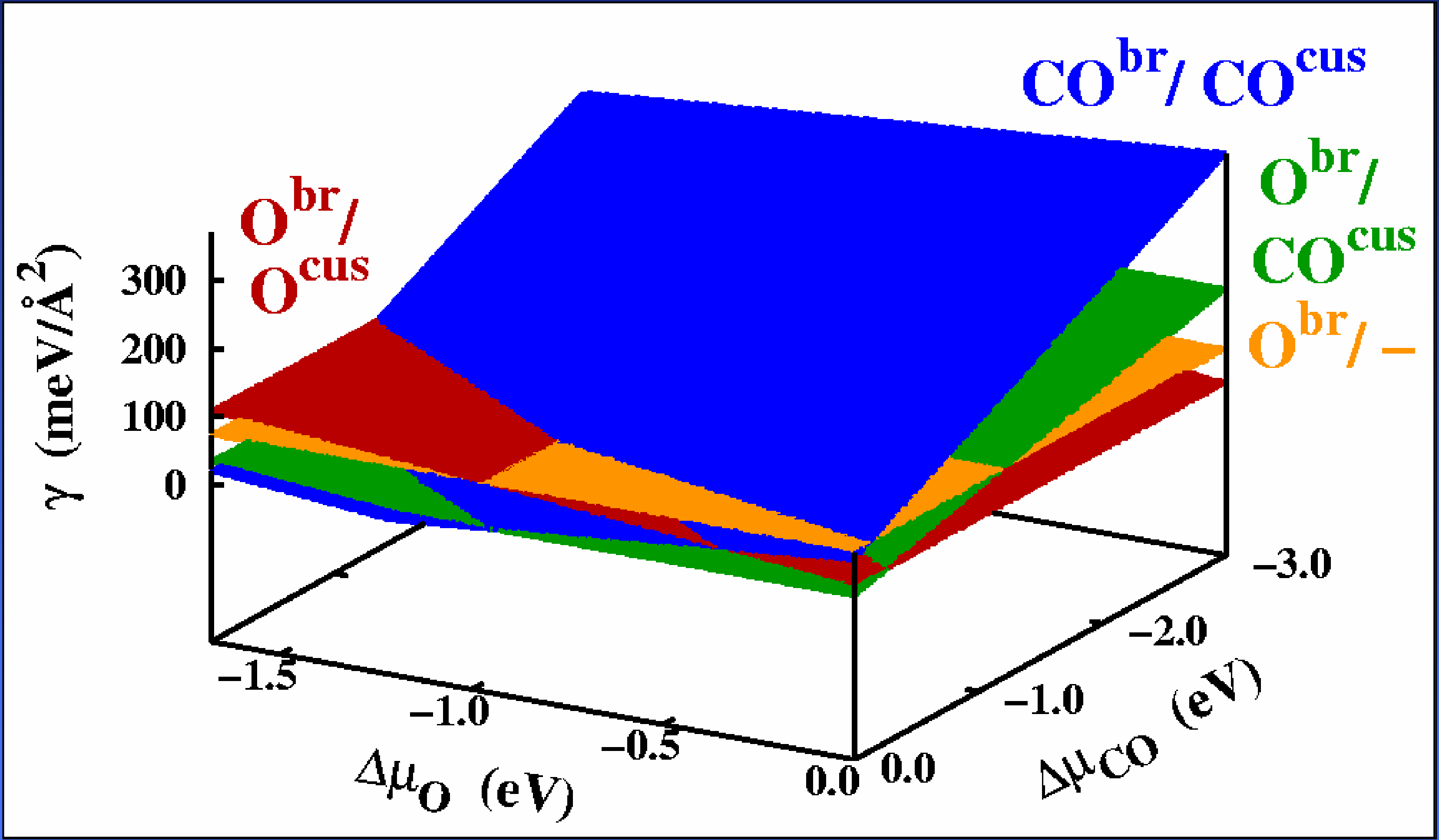
cus site

bridge site

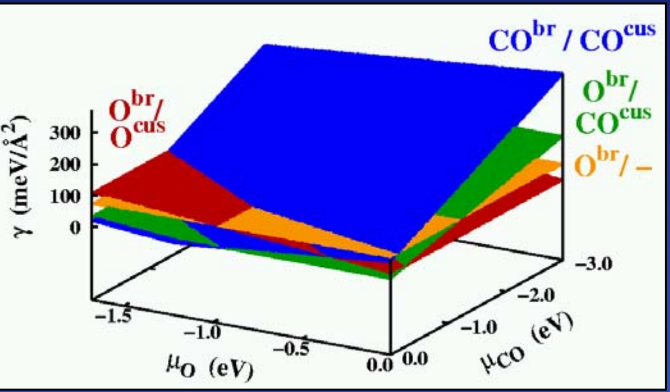
O

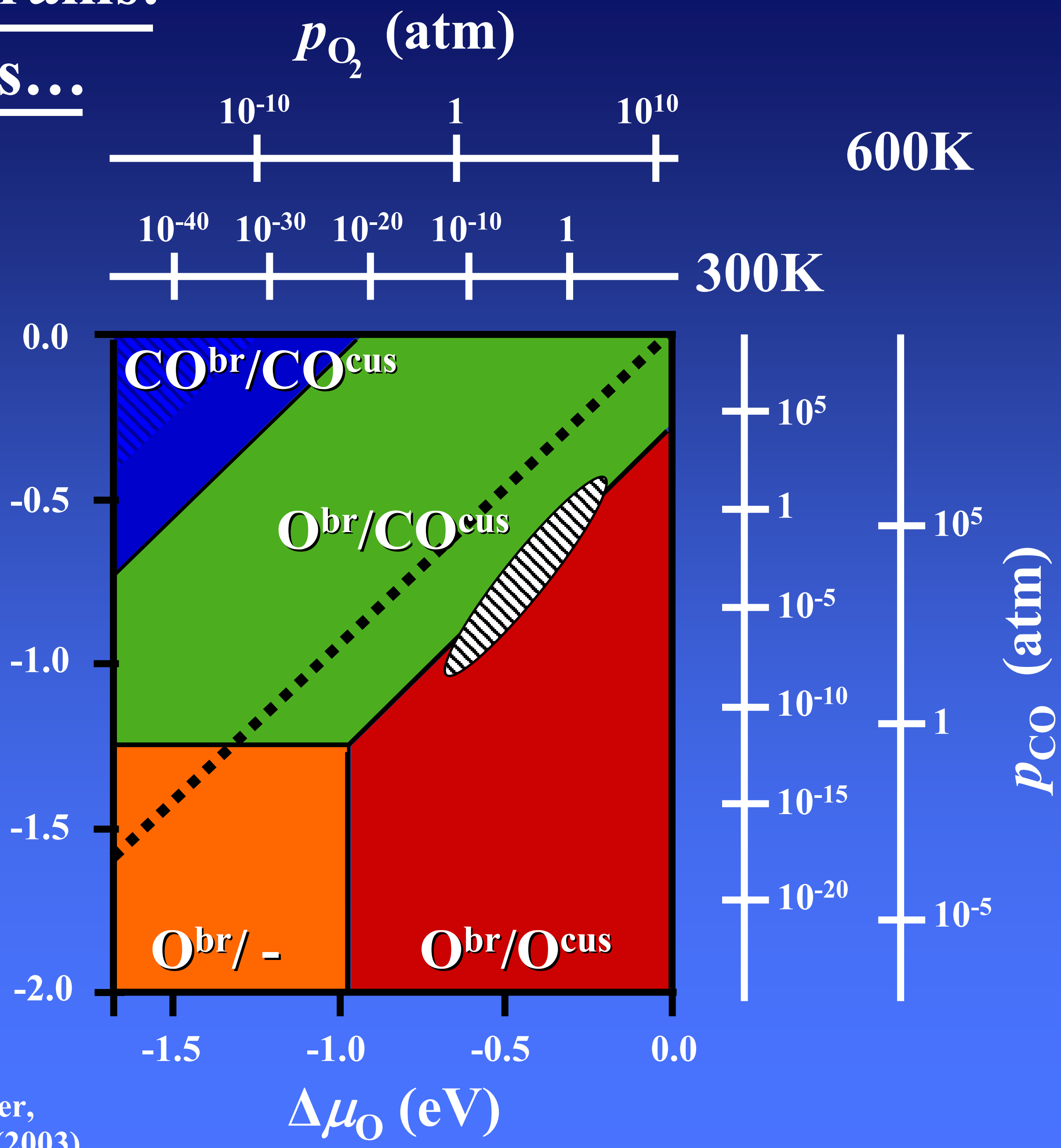
Ru

Surface free energy in a (O_2, CO) gas phase



Surface phase diagrams: towards catalysis…





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

In short:

By means of direct computation of free energies and the concept of reservoirs we can

- extend regular DFT to finite (*T,p*)
- treat surfaces in equilibrium with a realistic gas phase
- get a first idea about the surface composition and structure of surfaces in reactive environments („constrained equilibrium“)

Major limitations:

- we cannot predict a stable surface structure
- no account of kinetic effects

III. Exploration of configuration space: Monte Carlo simulations and lattice gas Hamiltonians

Understanding Molecular Simulation,
D. Frenkel and B. Smit, Academic Press (2002)

A Guide to Monte Carlo Simulations in Statistical Physics,
D.P. Landau and K. Binder, Cambridge Univ. Press (2000)

Statistical mechanics in a nutshell

A many-particle system will flow through its huge phase space, fluctuating through all microscopic states consistent with the constraints imposed on the system. For an isolated system with fixed energy *E* and fixed size *V,N* (microcanonic ensemble) these microscopic states are all equally likely at thermodynamic equilibrium (i.e. equilibrium is the most random situation).

Canonic ensemble (constant temperature):

Partition function $Z = Z(T,V) = \sum_i \exp(-E_i / k_B T)$ ⇒ **Boltzmann-weighted sum over all possible fluctuations**

⇒ $F = - k_B T \ln(Z)$

- In our case, the configuration space is spanned by all possible (continuous) positions r_N of the N atoms in the sample:

$$Z = \int dr^N \ \exp\left(- E(r_1,r_2,\dots,r_N) / k_B T\right)$$

- The average value of any observable A at temperature T in this ensemble is then

$$\langle A \rangle = 1/Z \int dr^N \ A(r_1,r_2,\dots,r_N) \exp\left(-E(r_1,r_2,\dots,r_N) / k_B T\right)$$

Evaluating high-dimensional integrals: Monte Carlo techniques

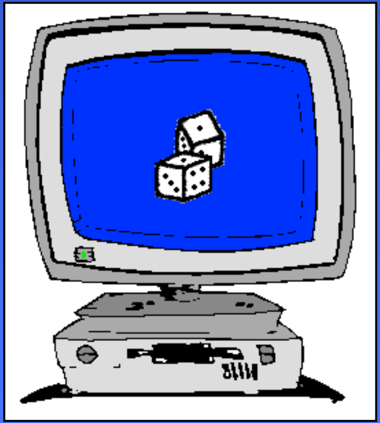
$$\langle A\rangle = 1/Z \int dr^N \; A(r_1,r_2,\ldots,r_N)\, \exp\left(-E(r_1,r_2,\ldots,r_N) / k_B T\right)$$

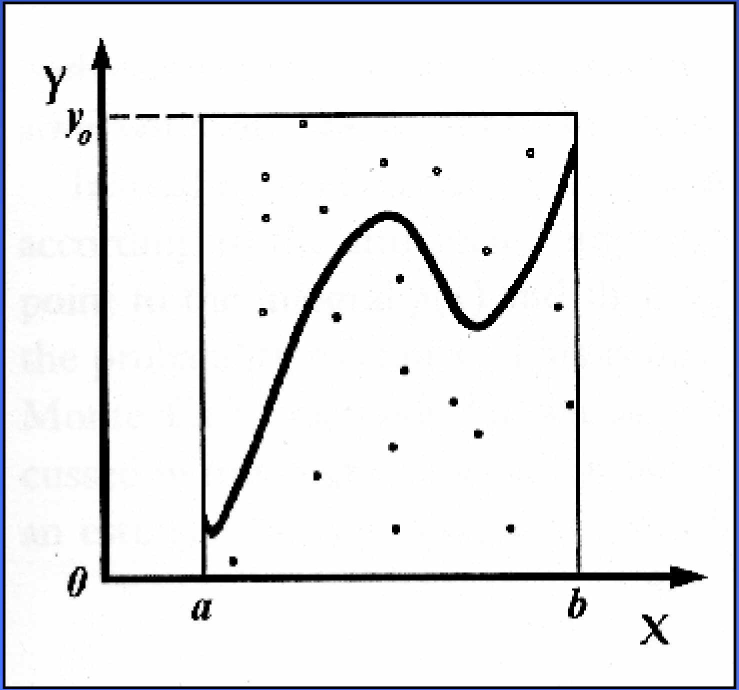
Problem:

- numerical quadrature (on a grid) rapidly unfeasible
- scales with: (no. of grid points)^N
- e.g.: 10 atoms in 3D, 5 grid points: $5^{30} \sim 10^{21}$ evaluations

Alternative:

- random sampling (Monte Carlo)



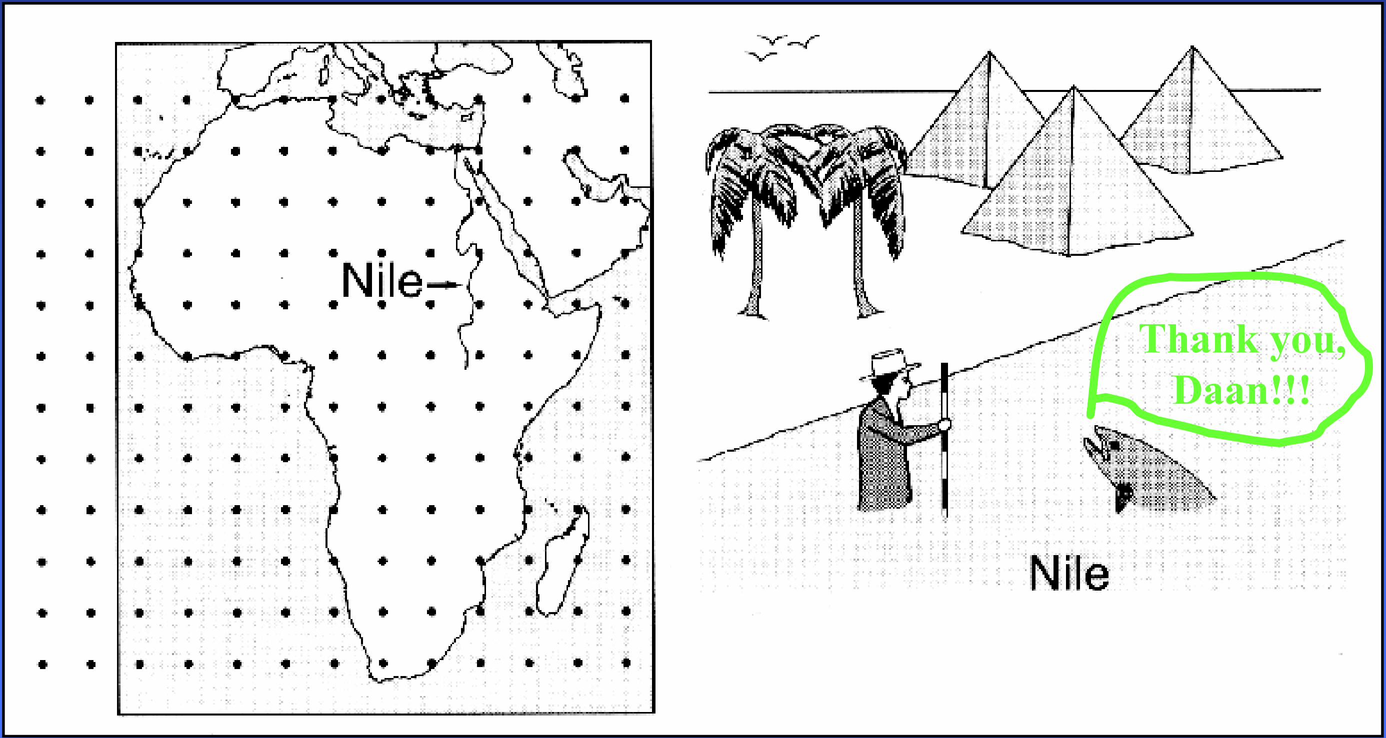


Example for integration by simple sampling

Finding a needle in a haystack: Importance sampling

$$\langle A \rangle = 1/Z \int dr^N \; A(r_1,r_2,\ldots,r_N)\,\exp\!\left(-E(r_1,r_2,\ldots,r_N)/k_BT\right)$$

Measuring the depth of the Nile



- Many evaluations where integrand vanishes
- Need extremely fine grid (very inefficient)

- Do random walk, and reject all moves that bring you out of the water
- Provides average depth of Nile, but NOT the total area!!

Specifying "getting out of the water": The Metropolis algorithm

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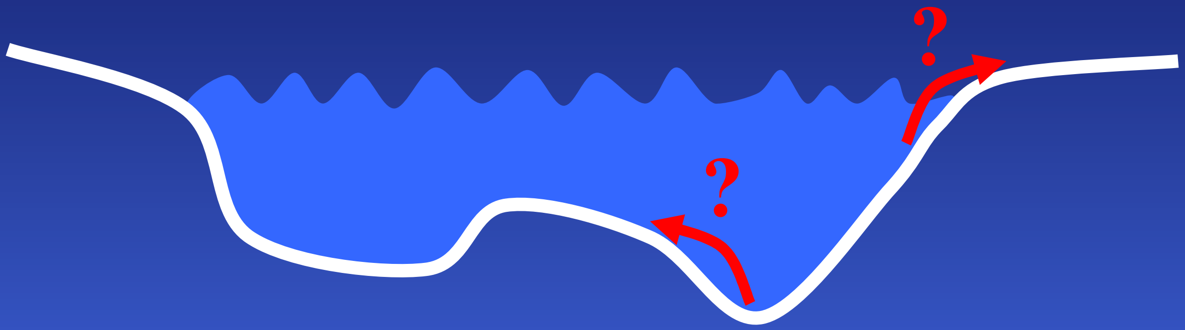


$E_{\text{trial}} < E_{\text{present}}$: accept

$E_{\text{trial}} > E_{\text{present}}$: accept with probability $\exp[-(E_{\text{trial}}-E_{\text{present}}) / k_B T]$

Some remarks:

- With this definition, Metropolis fulfills „*detailed balance*" and thus samples a canonic ensemble
- If temperature T is steadily decreased during simulation, upward moves become less likely and one ends up with an efficient ground state search („simulated annealing")

In short:

Modern importance sampling Monte Carlo techniques allow to

- efficiently evaluate the high-dimensional integrals needed for evaluation of canonic averages
- properly explore the configuration space, and thus configurational entropy is intrinsically accounted for in MC simulations

Major limitations:

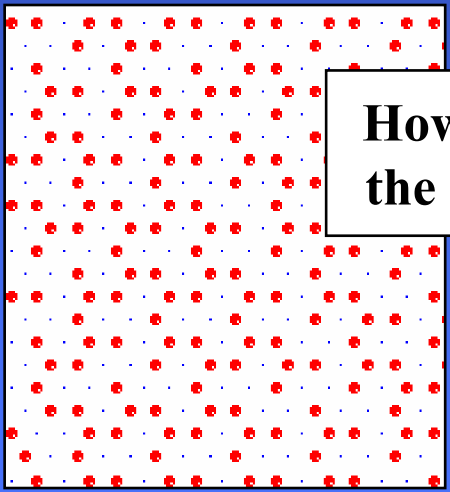
- still need easily $10^5 – 10^6$ total energy evaluations
- this is presently an unsolved issue. First steps in the direction of true „*ab initio* Monte Carlo“ are only achieved using lattice models

A very simple lattice system: O / Ru(0001)

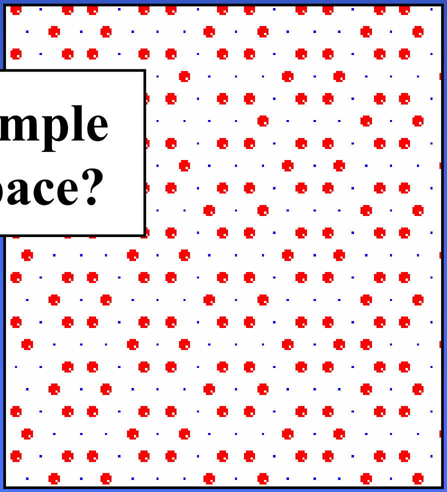
- Consider only adsorption into hcp sites (for simplicity)
- Simple hexagonal lattice, one adsorption site per unit cell
- Questions: which ordered phases exist ?
                    order-disorder transition at which temperature ?

Configuration space comprises:

disordered structures



ordered structures
(arbitrary periodicity)



How can we then sample the configuration space?

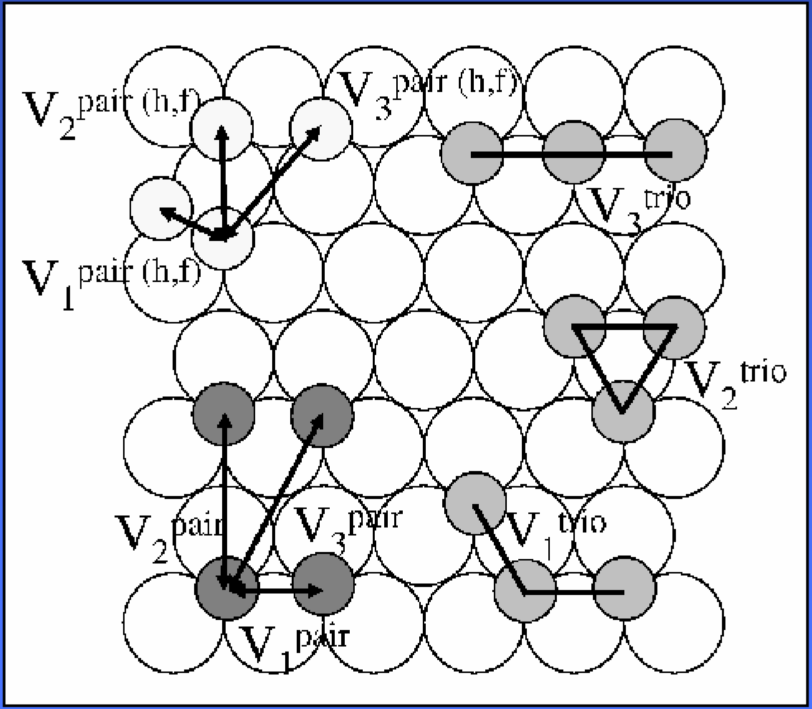
BUT: only periodic structures accessible to direct DFT,
and supercell size quite limited

Lattice gas Hamiltonians / Cluster expansions

Expand total energy of arbitrary configuration in terms of lateral interactions

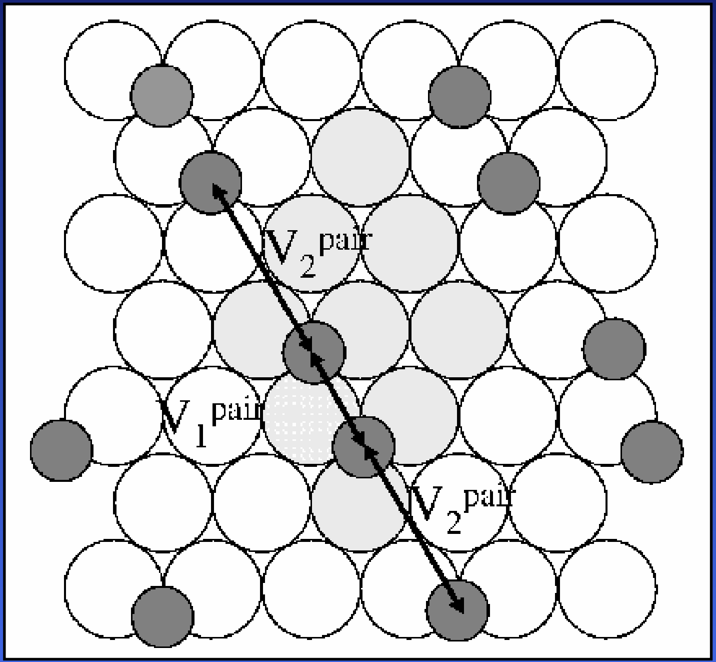
$$E^{\text{latt}} = \sum_i E_o + 1/2 \sum_{i,j} V^{\text{pair}}(d_{ij})\, \sigma_i\, \sigma_j + 1/3 \sum_{i,j,k} V^{\text{trio}}(d_{ij},d_{jk},d_{ki})\, \sigma_i\, \sigma_j\, \sigma_k + \dots$$

- Algebraic sum (very fast to evaluate)
- Ising, Heisenberg models
- Conceptually easily generalized to
    - multiple adsorbate species
    - more complex lattices (different site types etc.)



…but how can we get the lateral interactions from DFT?

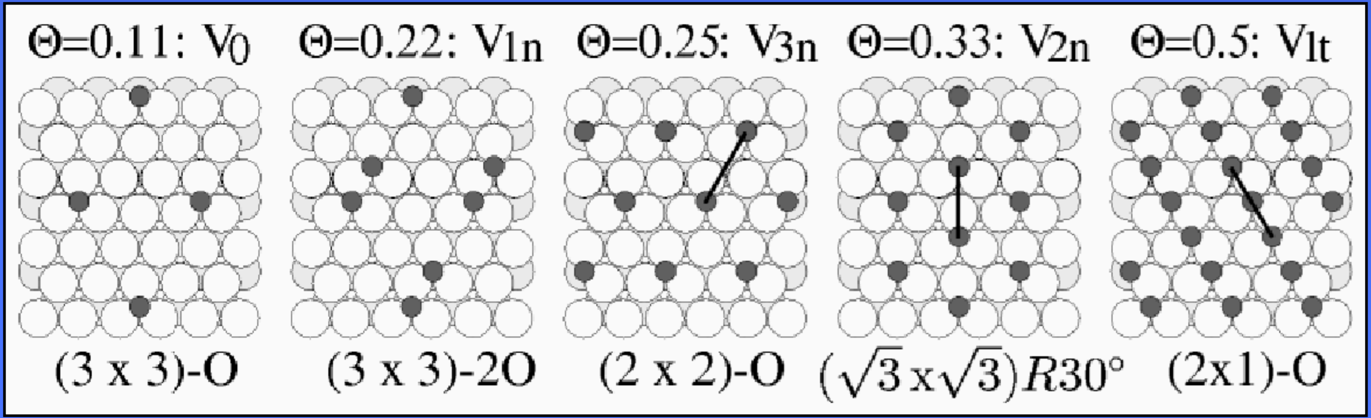
LGH parametrization through DFT



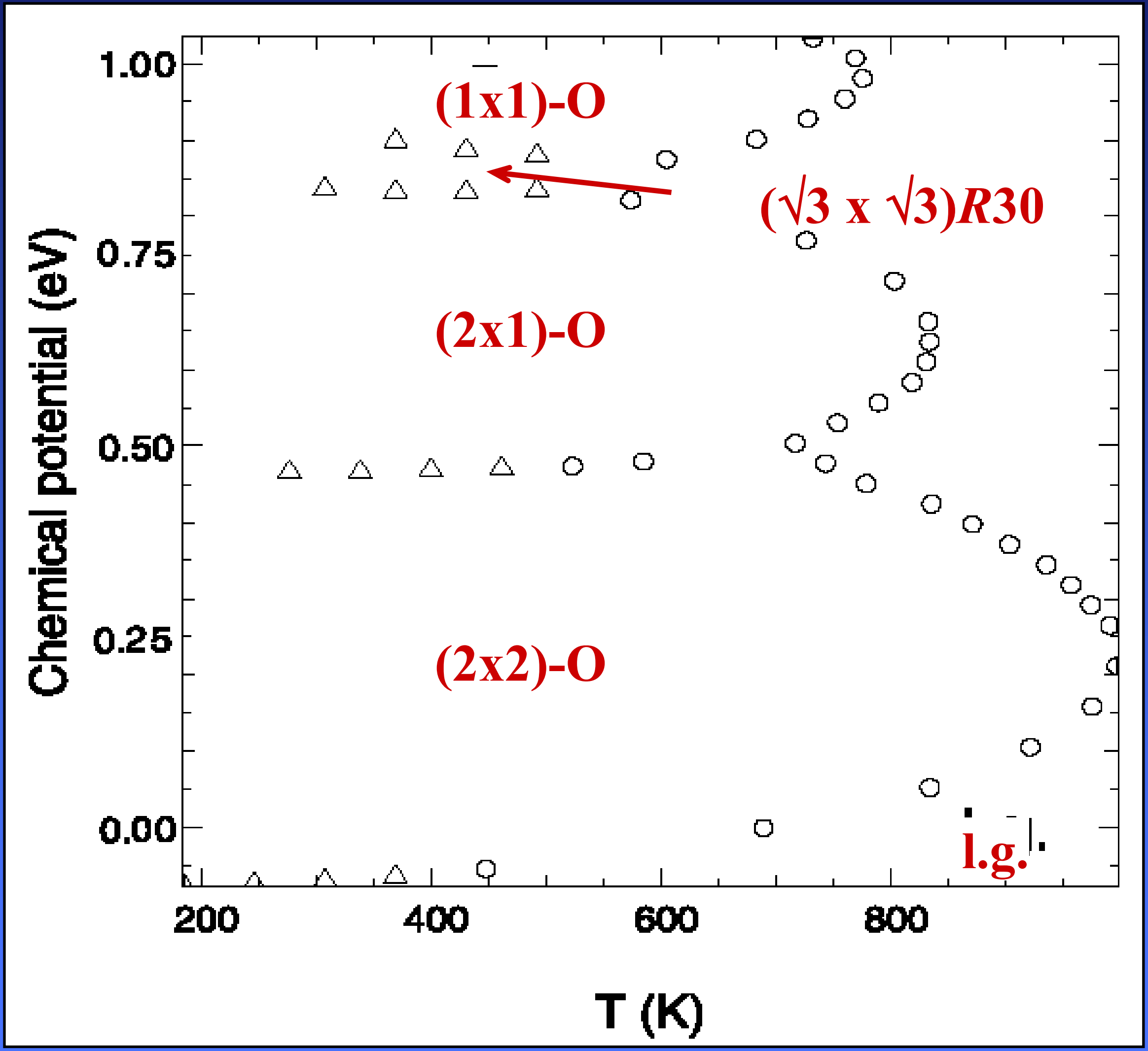
Since isolated clusters not compatible with supercell approach, exploit instead the interaction with supercell images in a systematic way:

- **Compute many ordered structures**
- **Write total energy as LGH expansion**
- **Set up system of linear equations**
- **„Invert“ to get lateral interactions**

e.g.
O / Ru(0001)



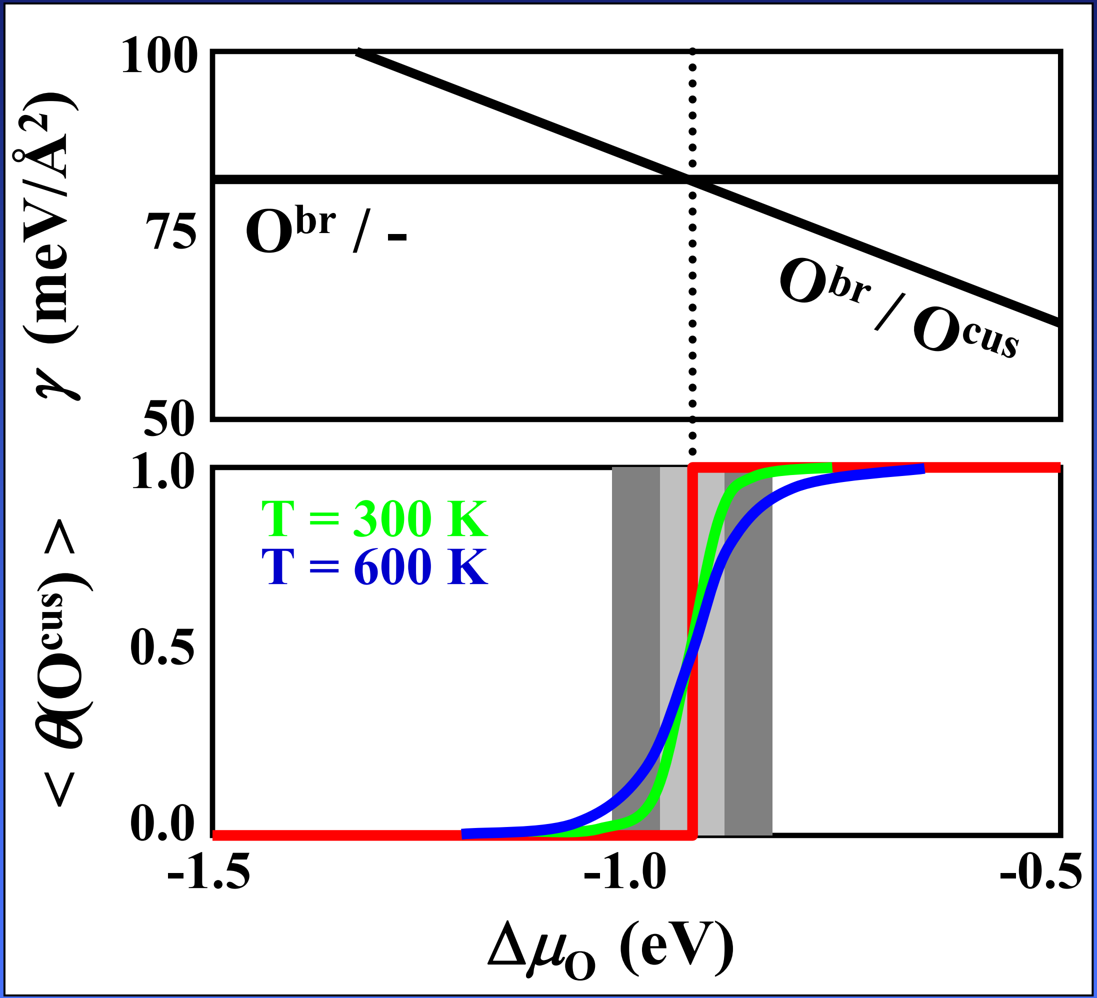
Surface phase diagram for O/Ru(0001)



C. Stampfl *et al*., Phys. Rev. Lett. 83, 2993 (1999)

Configurational entropy and phase transitions

e.g. O at $RuO_2(110)$

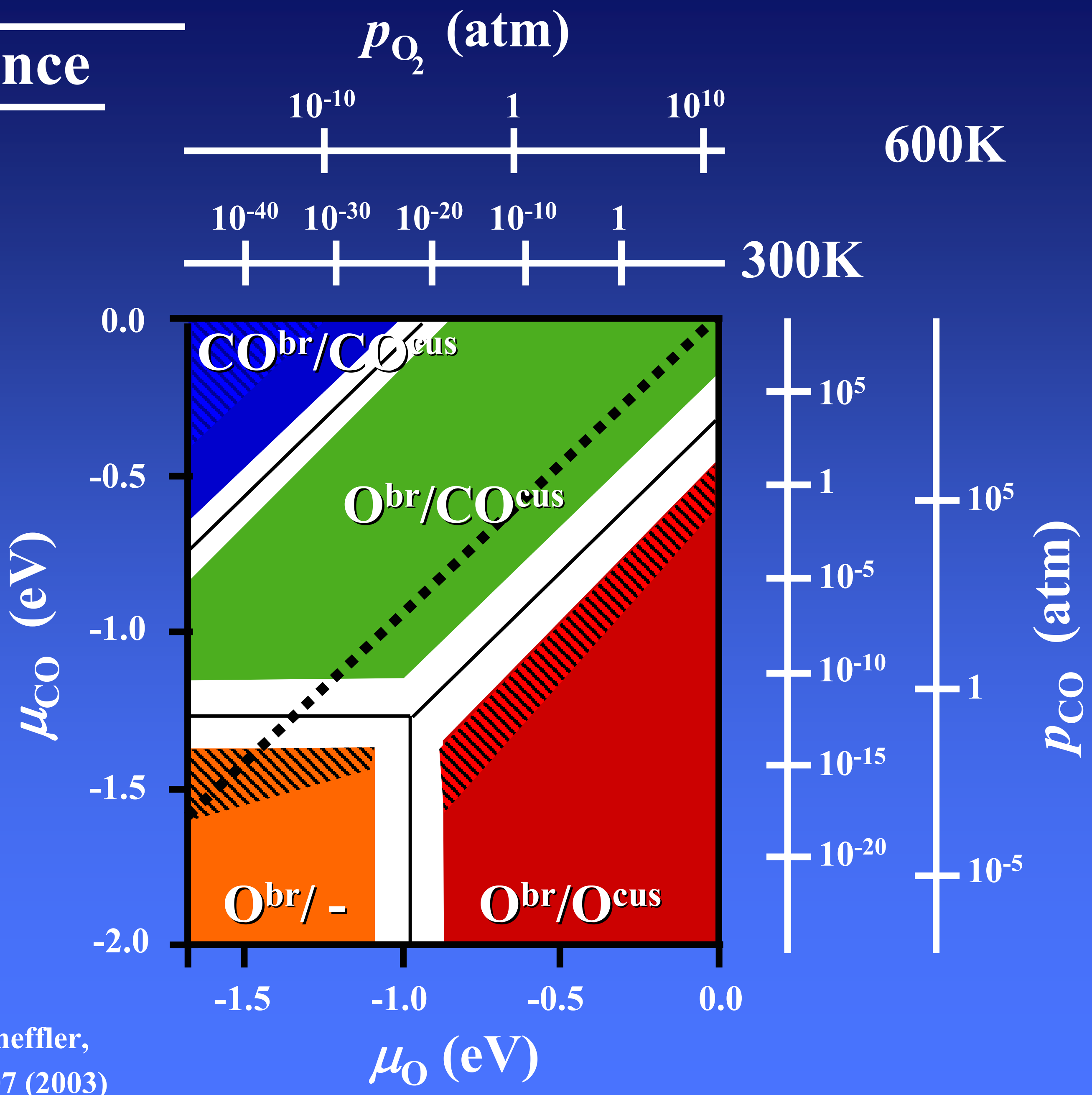


K. Reuter and M. Scheffler, Phys. Rev. B 65, 035406 (2002)

Configurational entropy smears out phase transitions

Particular relevance of phase coexistence regions ?!

e.g. O and CO at $RuO_2(110)$



K. Reuter and M. Scheffler,
Phys. Rev. B 68, 045407 (2003)

In short:

DFT parametrized lattice gas Hamiltonians enable

- efficient sampling of configurational space
- parameter-free prediction of phase diagrams
- first treatment of disordered structures

Major limitations:

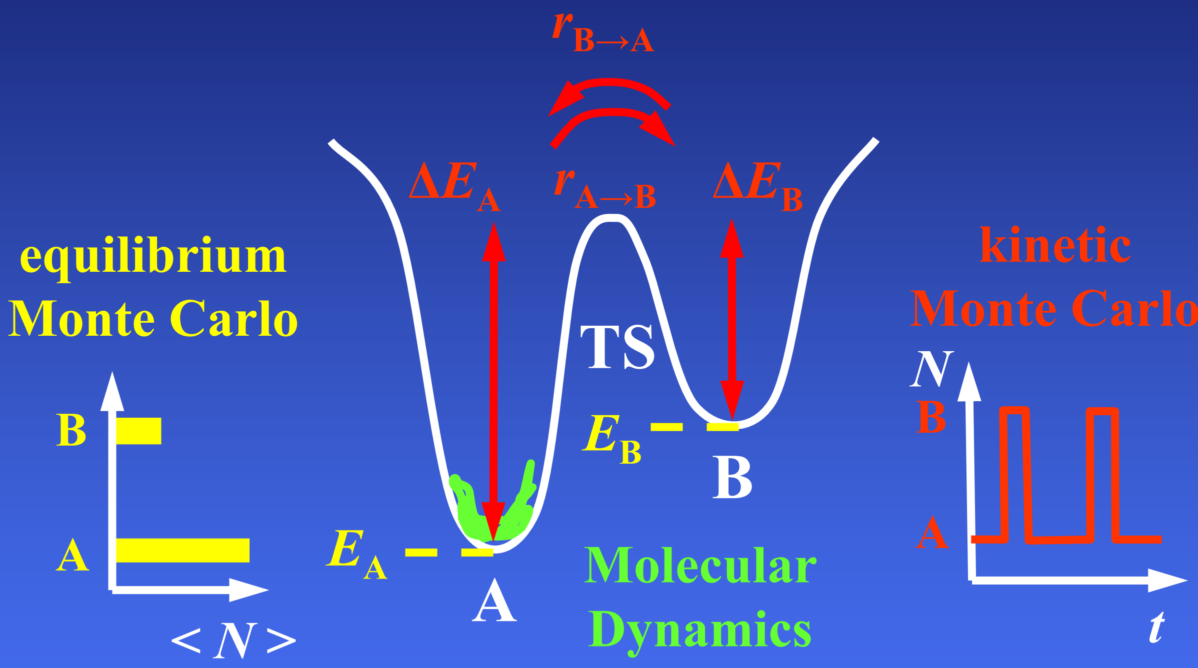
- systematics / convergence of LGH expansion
- restricted to systems that can be mapped onto a lattice
- expansion rapidly very cumbersome for complex lattices, multiple adsorbates, at defects/steps/etc.

IV. Following a coarse-grained time evolution: Kinetic Monte Carlo simulations

Extending the Time Scale in Atomistic Simulation of Materials,
A.F. Voter, F. Montalenti, and T.C. Germann,
Annu. Rev. Mater. Res. 32, 321 (2002)

Theoretical Foundations of Dynamical Monte Carlo Simulations,
K.A. Fichthorn and W.H. Weinberg,
J. Chem. Phys. 95, 1090 (1991)

First-principles kinetic Monte Carlo simulations



equilibrium Monte Carlo

B

A

$< N >$

$r_{B \to A}$

$r_{A \to B}$

ΔE_A

ΔE_B

TS

E_A

E_B

A

B

Molecular Dynamics

kinetic Monte Carlo

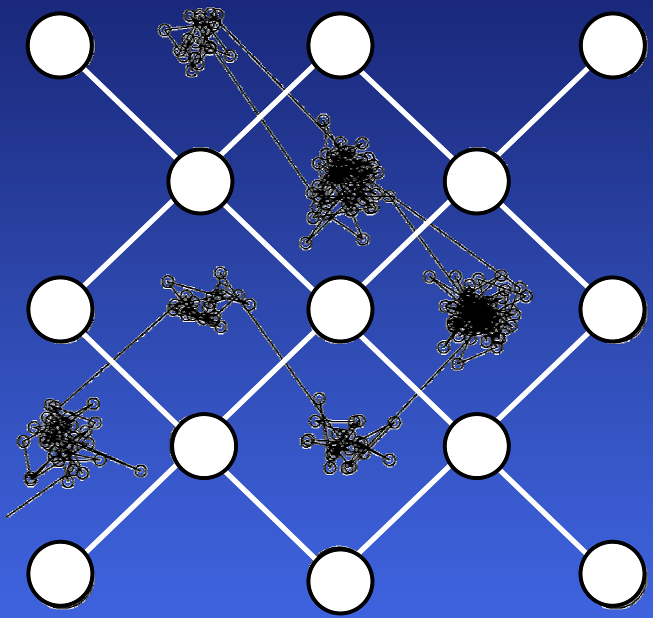
N

B

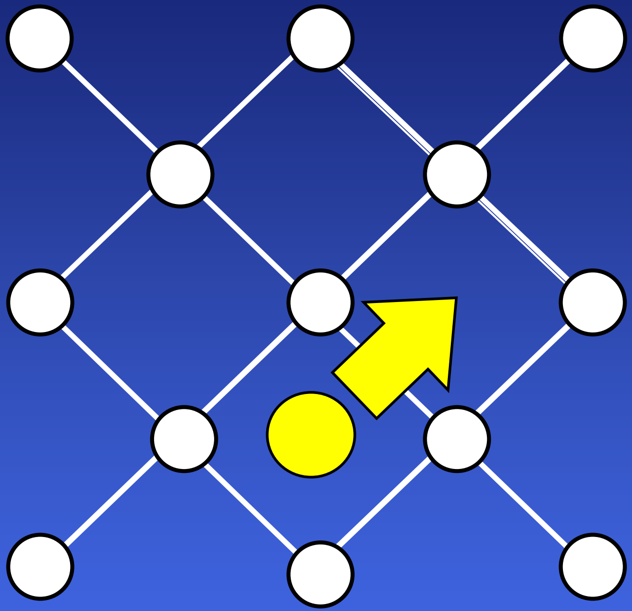
A

t

Kinetic Monte Carlo: essentially coarse-grained MD



Molecular Dynamics:
the whole trajectory

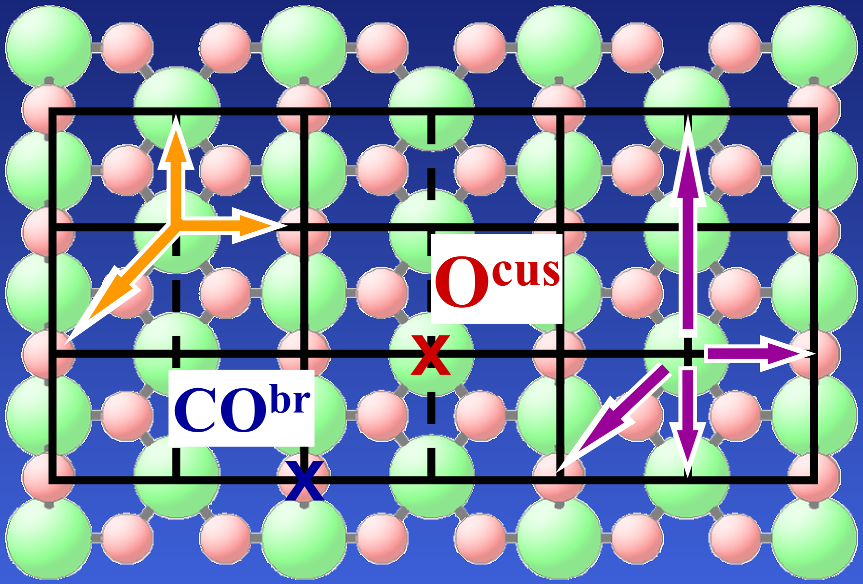


Kinetic Monte Carlo:
coarse-grained hops

ab initio MD:
up to 50 ps

ab initio kMC:
up to minutes

kMC in practice



i) Map onto a lattice

Rectangular unit-cell

Two site types: - br
- cus

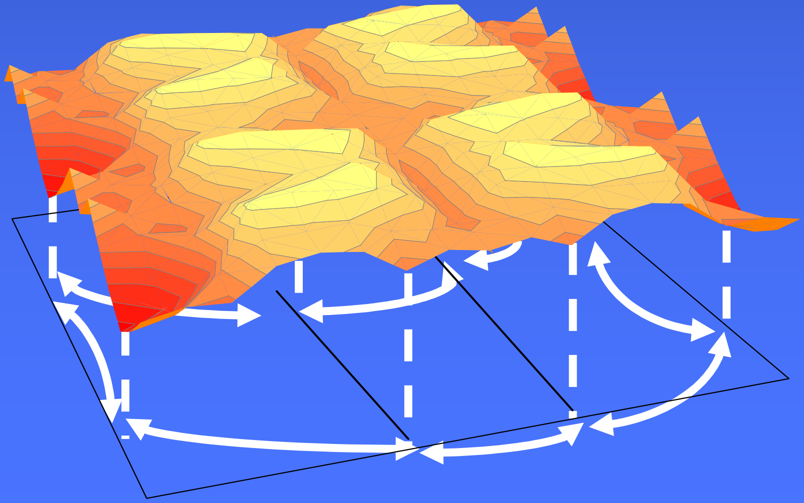
Sites can be:
- empty
- O (x)
- CO (x)

ii) Get process rates

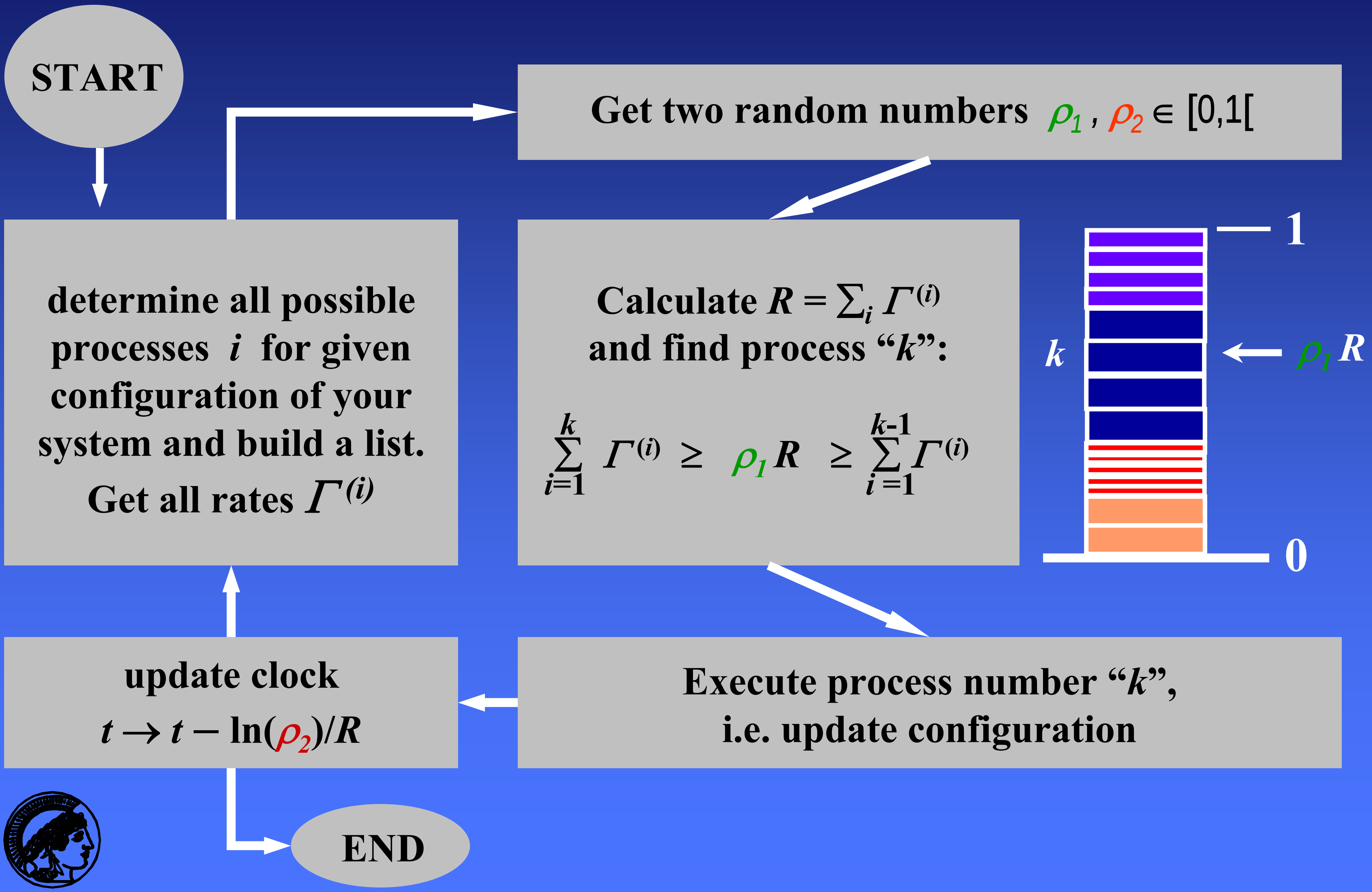
PES from density-functional theory
(FP-LAPW, GGA)

Transition state theory

$$\Gamma = kT/h\ Z_{TS}/Z_{IS}$$
$$= \Gamma_o \exp(-\Delta E/kT)$$



Flowchart of a kinetic Monte-Carlo simulation



START

determine all possible processes *i* for given configuration of your system and build a list. Get all rates $\Gamma^{(i)}$

Get two random numbers $\rho_1, \rho_2 \in [0,1[$

Calculate $R = \sum_i \Gamma^{(i)}$ and find process "*k*":

$$\sum_{i=1}^{k} \Gamma^{(i)} \geq \rho_1 R \geq \sum_{i=1}^{k-1} \Gamma^{(i)}$$

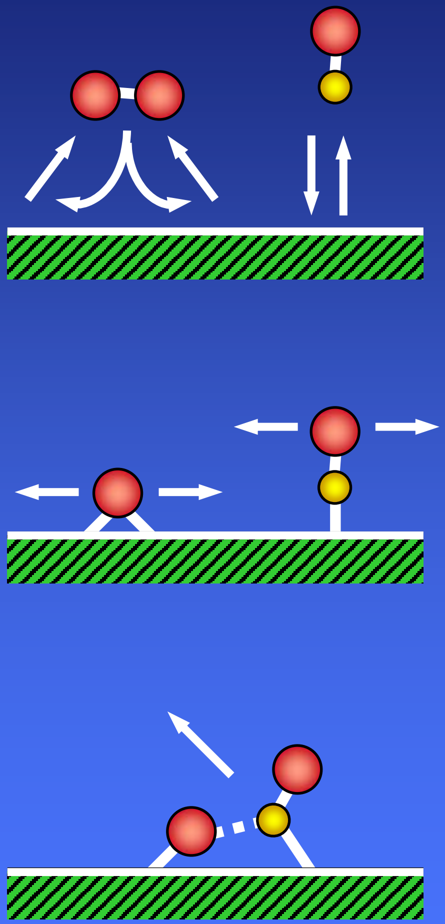
Execute process number "*k*", i.e. update configuration

update clock

$t \rightarrow t - \ln(\rho_2)/R$

END

kMC events for CO oxidation over $RuO_2(110)$



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

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

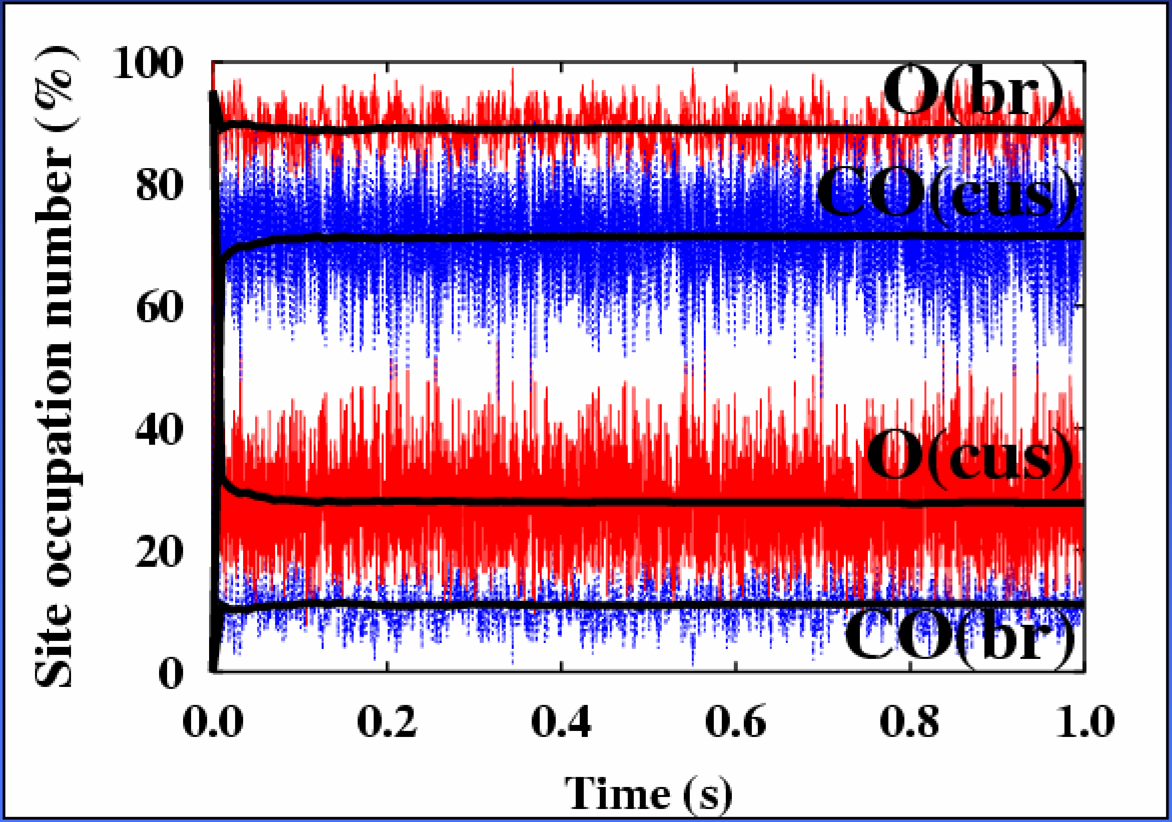
Diffusion:
hops to nearest neighbor sites
site and element specific
barrier from DFT (TST)
prefactor 10^{12} s^{-1} (generic)

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

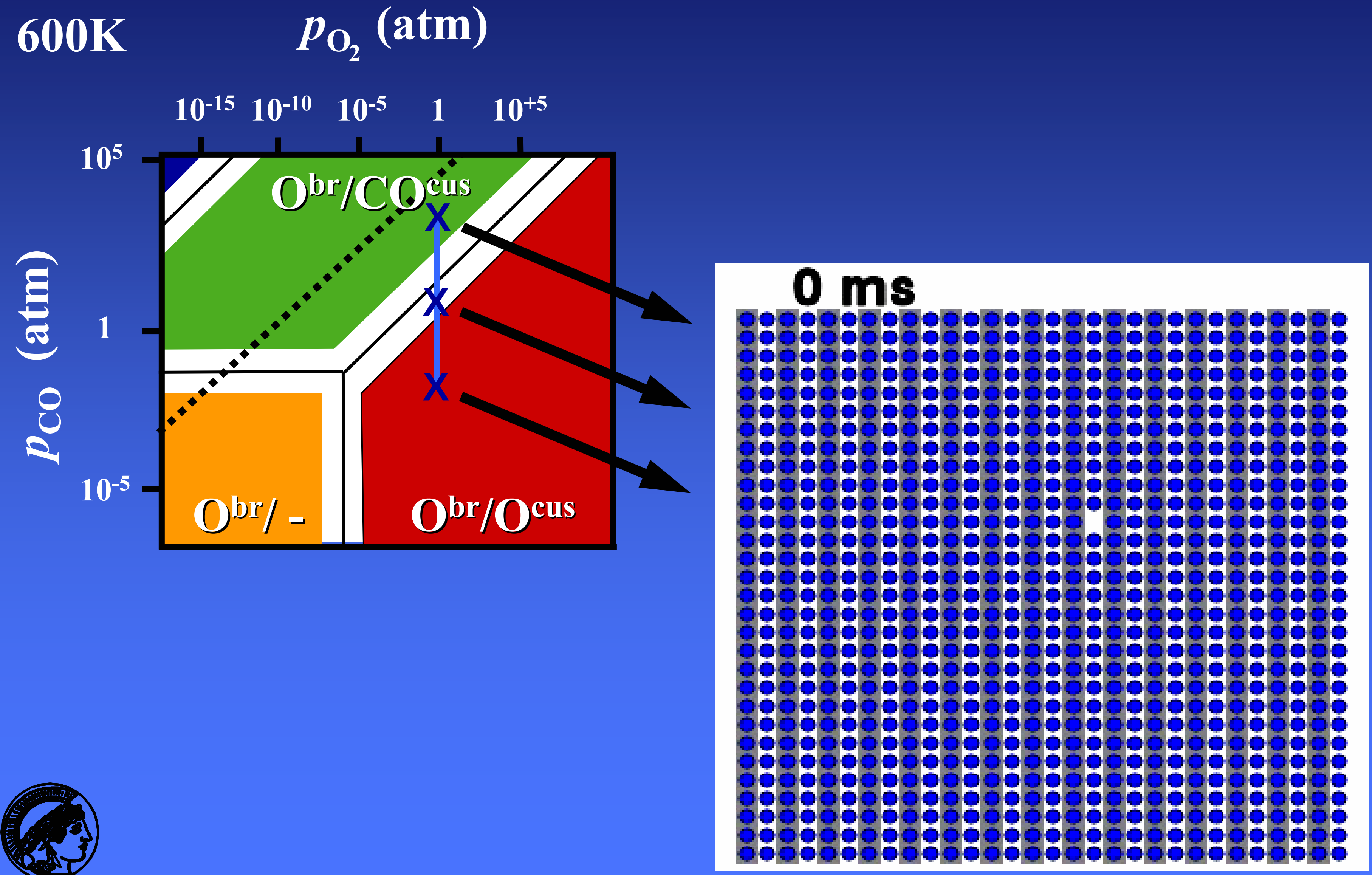
26 elementary processes considered

Reaching steady-state conditions: induction period

$T = 600$ K $p_{O_2} = 1$ atm $p_{CO} = 20$ atm

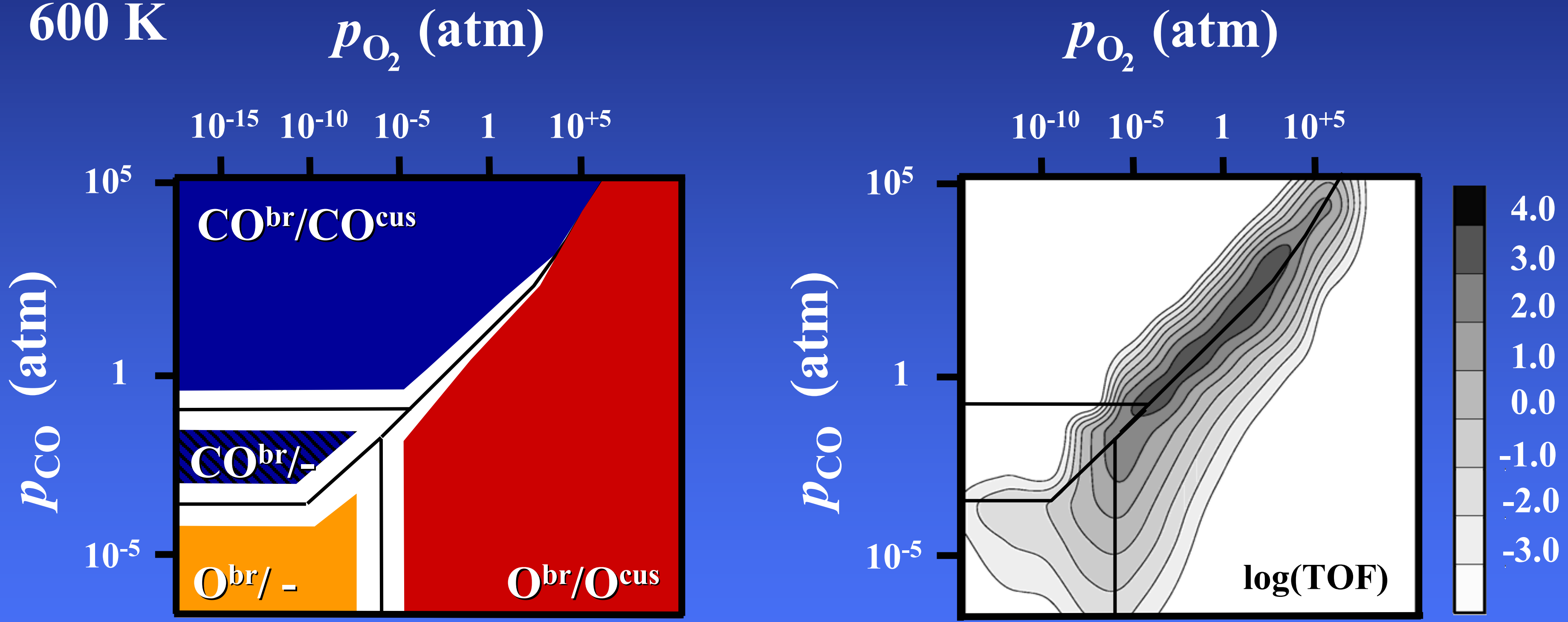


Steady-state surface population



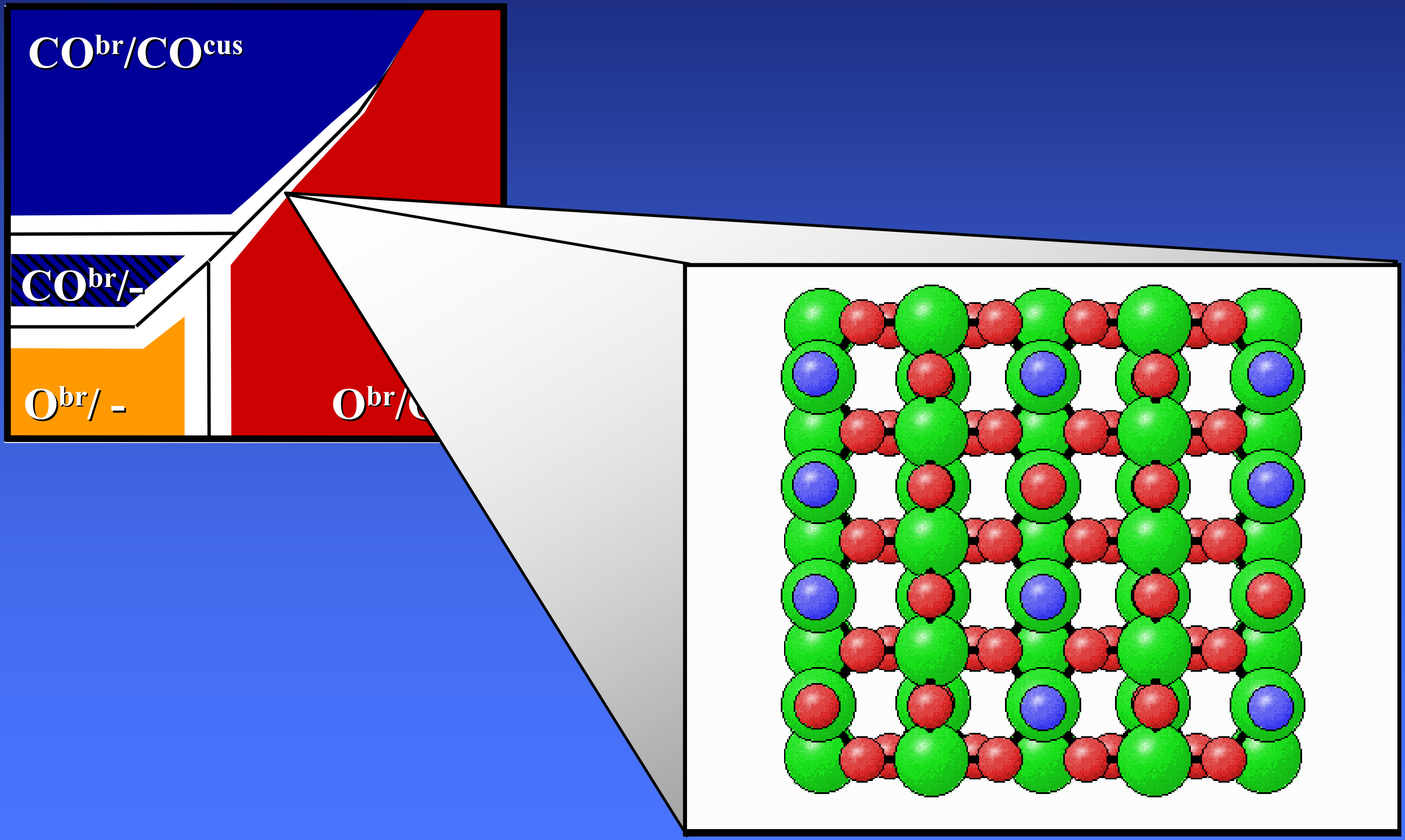
A (p_{CO}, p_{O_2})-map of catalytic activity

600 K

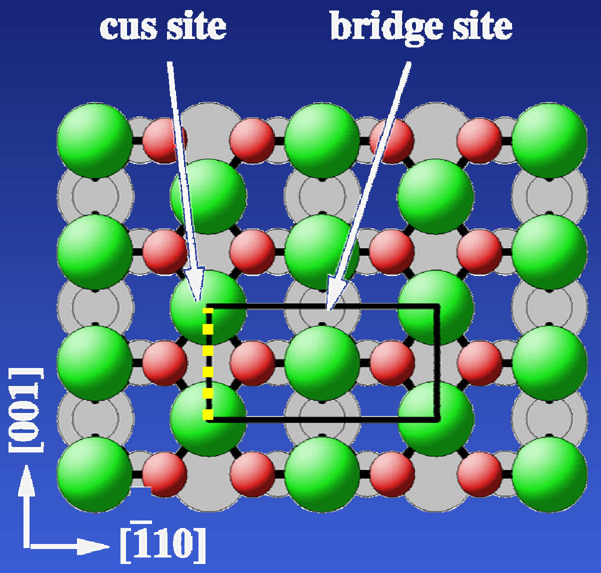


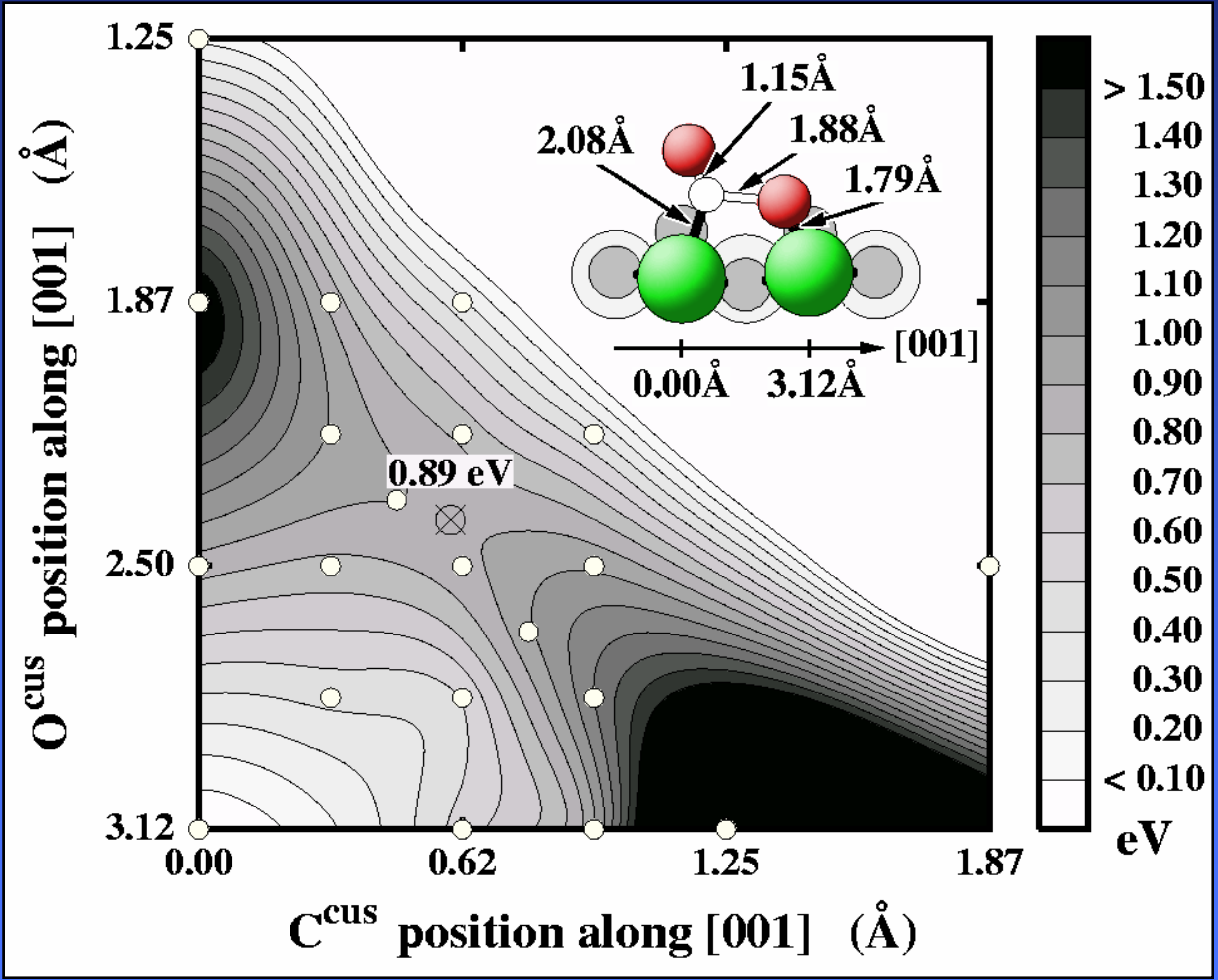
K. Reuter, D. Frenkel and M. Scheffler, Phys. Rev. Lett. 93, 116105 (2004)

Low barrier mechanism: $CO^{cus} + O^{cus} \rightarrow CO_2$



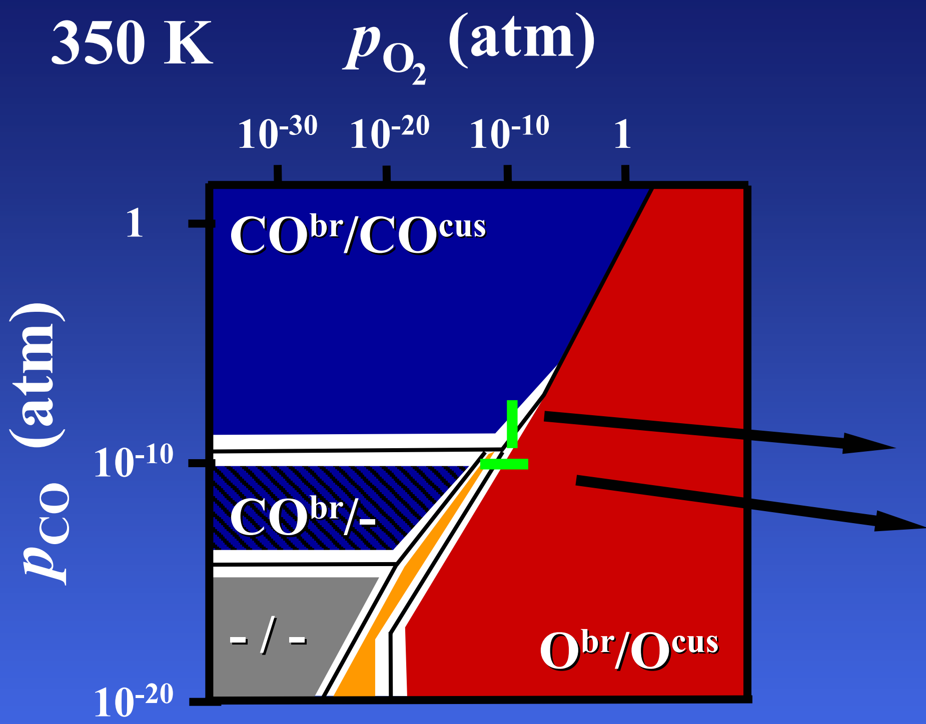
$CO^{cus} + O^{cus} \rightarrow CO_2$: Reaction barrier

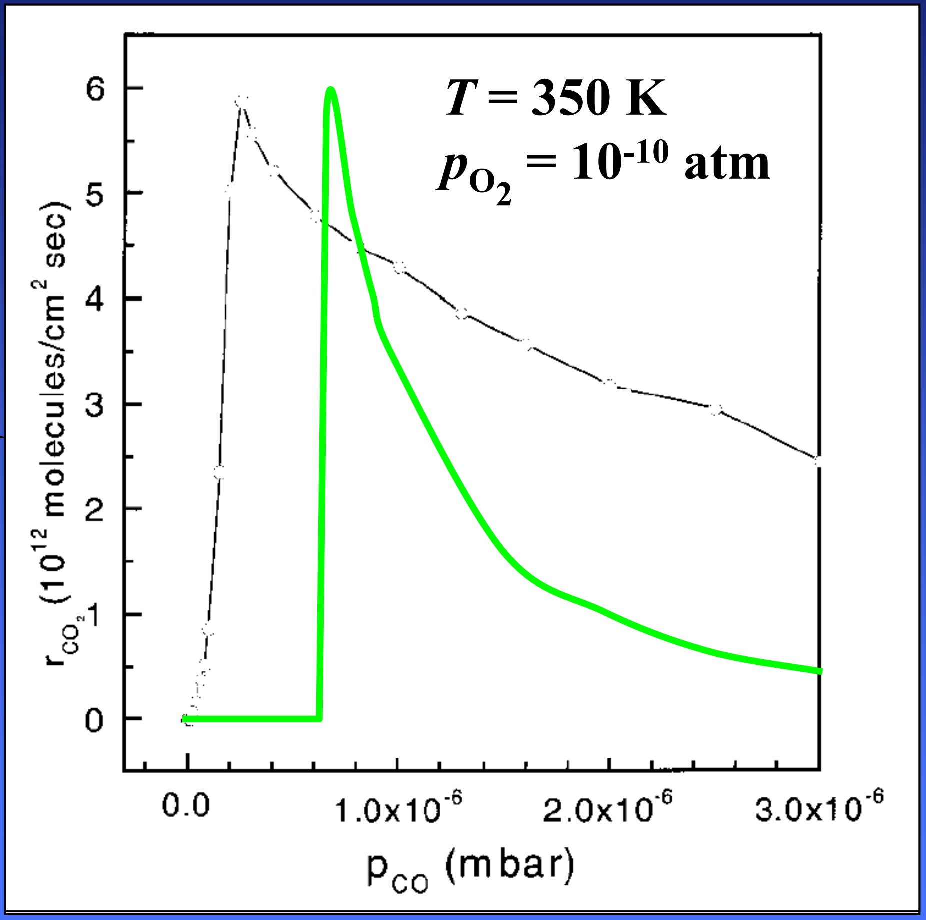


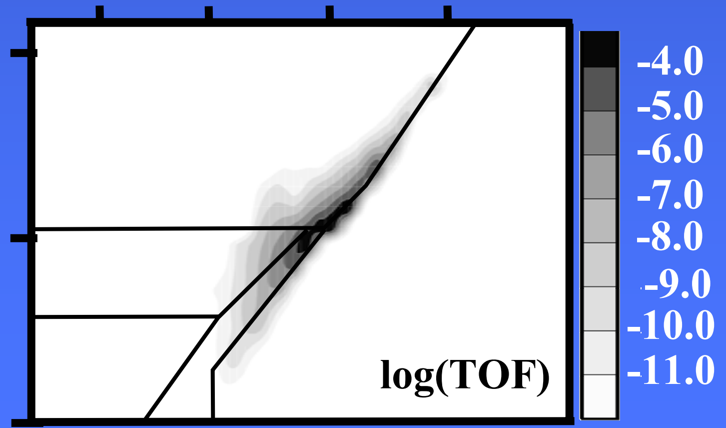


K. Reuter and M. Scheffler, Phys. Rev. B 68, 045407 (2003)

…and how about experiment?







J. Wang, C.Y. Fan, K. Jacobi, and G. Ertl,
J. Phys. Chem. B 106, 3422 (2002)

In short:

With *ab initio* kMC

- we can follow the time evolution of a system up to time scales of seconds
- we can efficiently treat the interplay of a larger number of elementary processes
- we typically find that a much larger number of processes is necessary for a quantitative modeling than employed in previous empirical kMC work

Major limitations:

- same restriction to simple lattice systems as LGH/MC
- fixed process list (currently mostly based on chemical intuition)
- accuracy of rates (DFT-TST)
- low speed-up, if very fast processes present

From micro to meso in catalysis research

Electronic Structure Theory **meets** **Thermodynamics**
Statistical mechanics

First-principles atomistic thermodynamics:

- **Knowledge of surface structure under stationary-reaction conditions**
- **First understanding about catalytically relevant phases**

First-principles kinetic Monte-Carlo:

- **Statistical interplay between manifold of elementary processes**
- **Parameter-free calculation of turnover frequencies**