The Abdus Salam
International Centre for Theoretical Physics

United Nations
Educational, Scientific and
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2145-18

Spring College on Computational Nanoscience

17 - 28 May 2010

At the Fifth Rung of Jacob's Ladder: A discussion of exact exchange plus local- and nonlocal-density approximations to the correlation functional

Matthias SCHEFFLER
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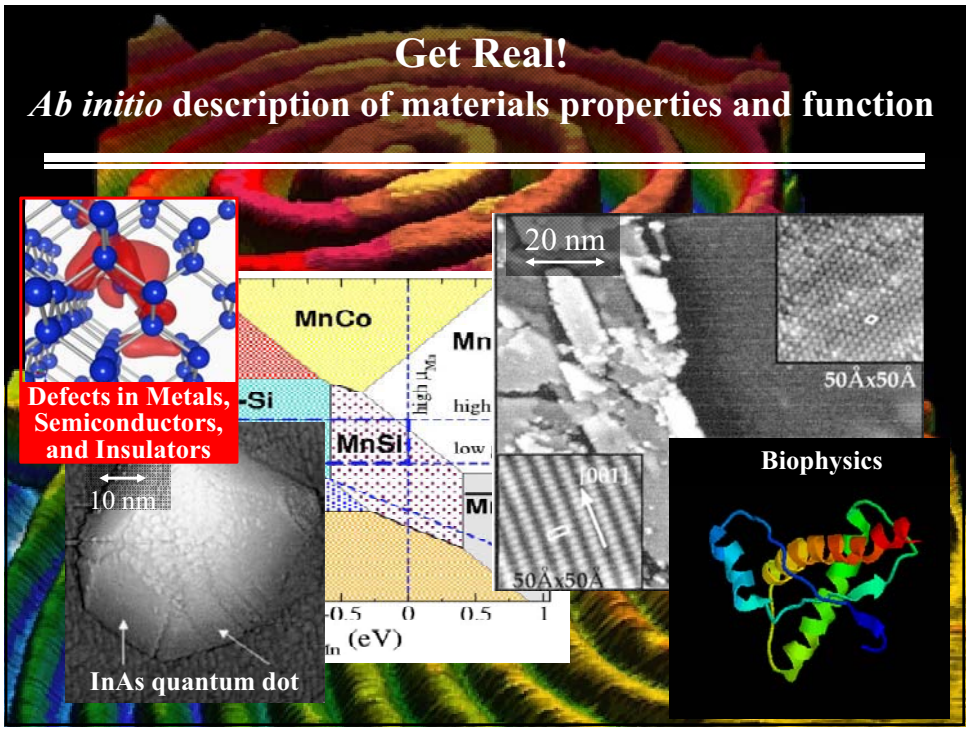
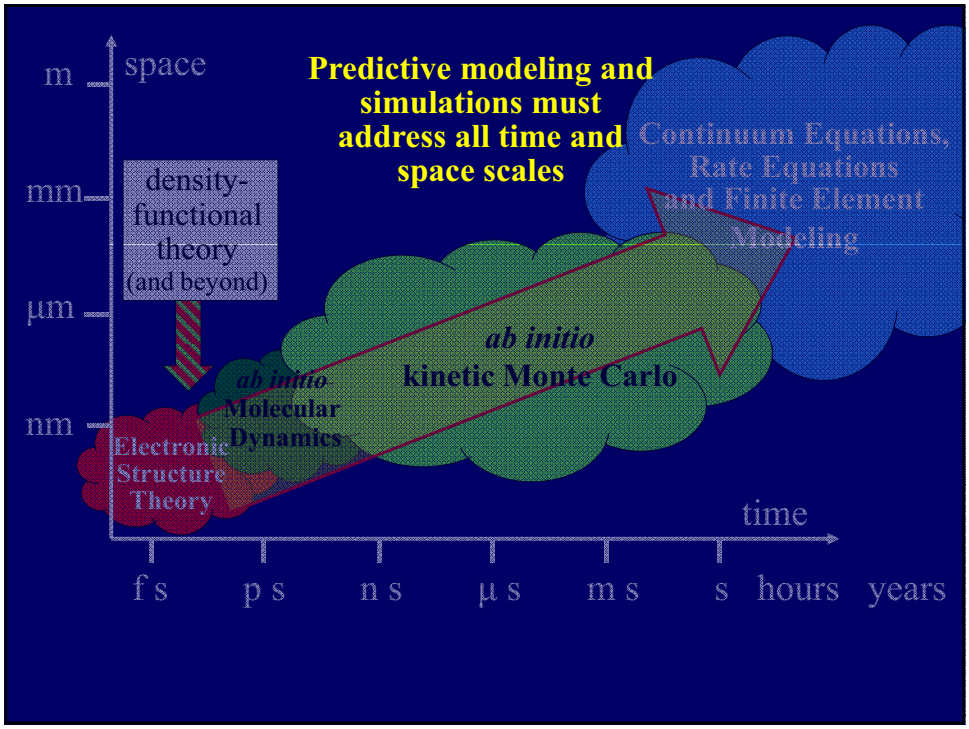
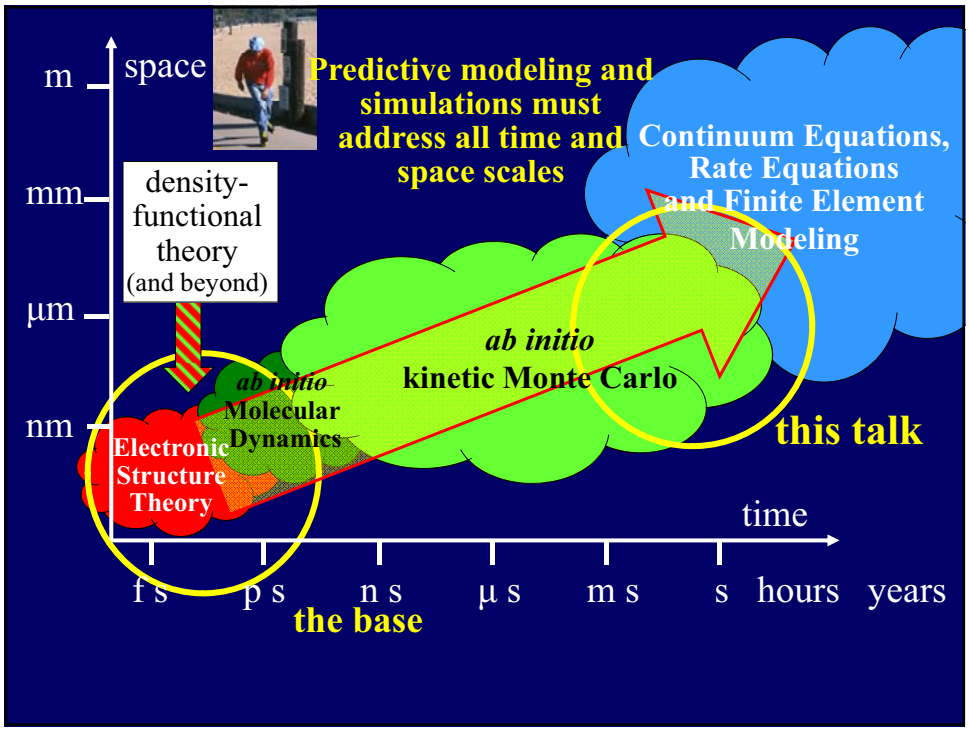
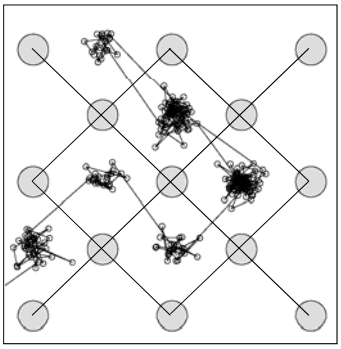

Get Real!
Ab initio description of materials properties and function
Defects in Metals, Semiconductors, and Insulators
10 nm
InAs quantum dot
MnCo
Mn
Si
MnSi
high
low
-0.5
0
0.5
1
(eV)
20 nm
50Åx50Å
[001]
50Åx50Å
Biophysics


m
space
mm
μm
nm
density-functional theory (and beyond)
Predictive modeling and simulations must address all time and space scales
Continuum Equations, Rate Equations and Finite Element Modeling
ab initio kinetic Monte Carlo
ab initio Molecular Dynamics
Electronic Structure Theory
time
f s
p s
n s
μ s
m s
s
hours
years

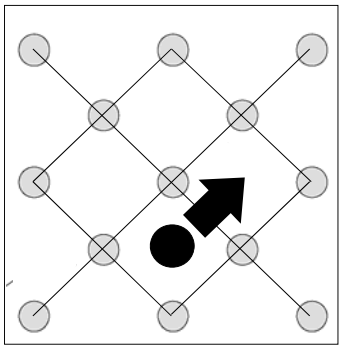


Kinetic Monte Carlo: Coarse-Graining Molecular Dynamics



Molecular Dynamics of Co on Cu(001): The whole trajectory.

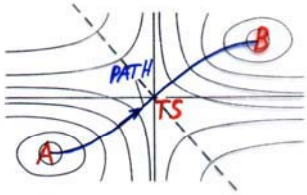
ab initio MD: up to 50 ps



Kinetic Monte Carlo simulation: Coarse-grained hops.

ab initio kMC: up to minutes

Transition State Theory



Transition state theory

$$\Gamma = \frac{k_B T}{h} exp\left(\frac{-\Delta F}{k_B T}\right)$$

$$\Delta F = -k_B T \, ln Z_{TS} + k_B T \, ln Z_A$$

$$\Gamma = \Gamma_0 \, exp\left(\frac{-\Delta E}{k_B T}\right)$$

$$\Gamma_0 = \frac{k_B T}{h} exp\left(\frac{\Delta S^{vib}}{k_B} - \frac{\Delta U^{vib}}{k_B T}\right)$$

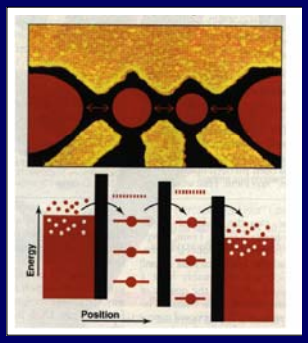
kMC Summary

- kMC is a coarse-grained technique for condensed-matter dynamics.
- It is a numerical solution of the master equation.
- It gives essentially the same information as MD -- but can simulate time spans $>10^{12}$ times longer.
- It can be linked to *ab initio* rate processes. Often transition state theory can be applied. Configurational entropy and resulting (kinetic) barriers are fully taken into account.

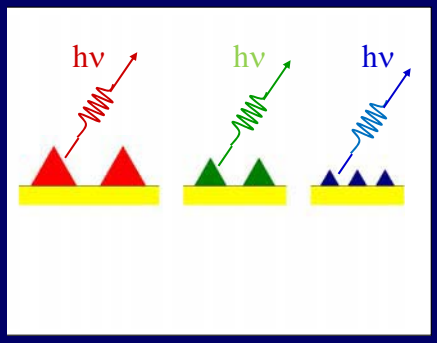
Self-Assembly of Nano-Scale Structures at Semiconductor Surfaces

Motivation:

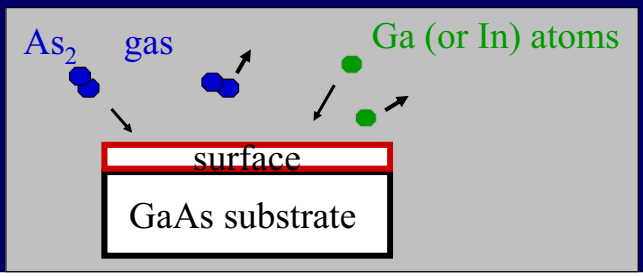
Single-electron transistor



LEDs and laser diodes



Microscopic processes controlling the growth -- Example: III-V semiconductors

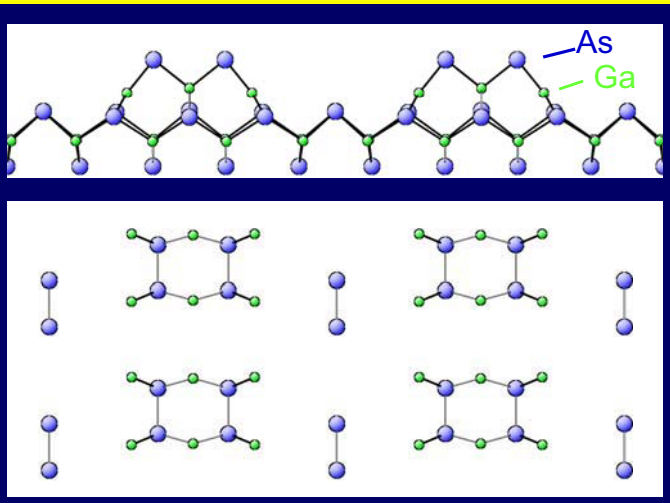


1) deposition of Ga and As
2) adsorption of Ga
3) diffusion of Ga
4) desorption of Ga
5) adsorption of As_2 ?
6) dissociation of As_2 ?
7) diffusion of As
8) desorption of As
9) island nucleation
10) growth

β2 Reconstruction of GaAs (001) (2x4) Unit Cell

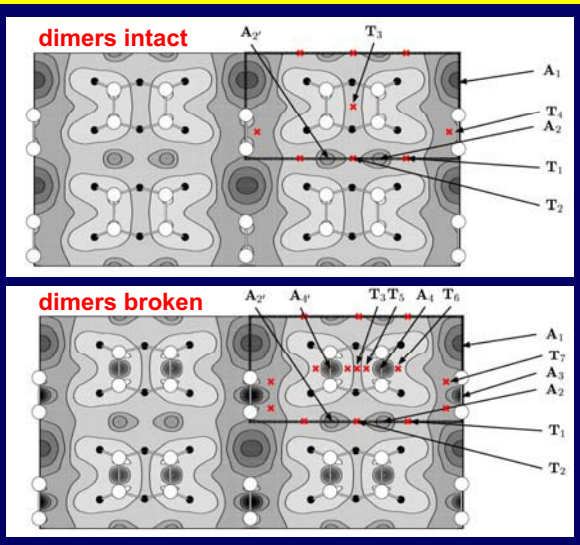
side view

top view



Total Energy of a Diffusing Ga Atom at GaAs (001)

top view



E_{A1} = -1.9 eV

E_{TS} = -1.5 eV

E_{A2} = -1.5 eV

E_{TS} = -1.3 eV

E_{A3} = -2.1 eV

E_{TS} = -1.3 eV

*A. Kley, P. Ruggerone, and M.S., PRL **79** (1997)*

Growth kinetics from first principles

-- example: III-V semiconductors --

1) Analysis of all possibly relevant processes using density-functional theory.

2) Calculate the rates of all important processes

$$\Gamma^{(i)} = \Gamma_0^{(i)} \exp\left(-\Delta E^{(i)} / k_B T\right)$$

3) Statistical approach to describe
   - deposition
   - diffusion
   - nucleation
   - growth

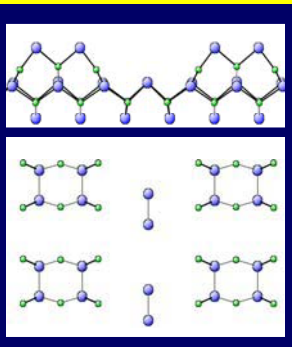
Peter Kratzer

➡ **kinetic Monte Carlo method**

Adsorption, diffusion, island nucleation, and growth of GaAs

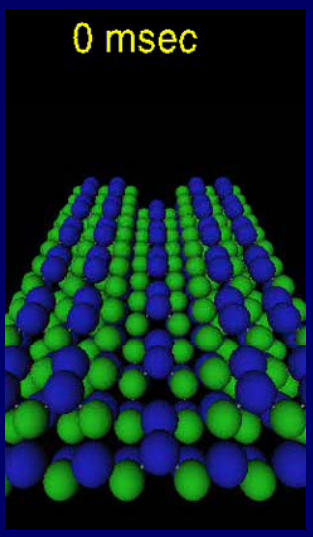
side view

top view



Ga

As



1/60 of the full simulation cell

As_2 pressure $\approx 1.33 \times 10^{-8}$ bar

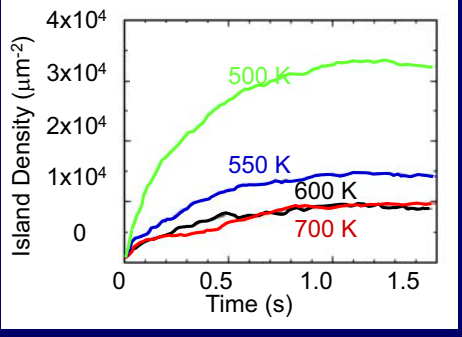
Ga deposition rate = 0.1 ML/s

$T = 700$ K

P. Kratzer & M. S., PRL 88, 036102 (2002)

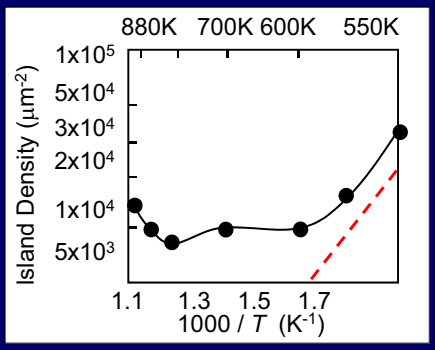
Island density

P. Kratzer & M. S., PRL 88, 036102 (2002)



As_2 pressure
= 1.33×10^{-8} bar

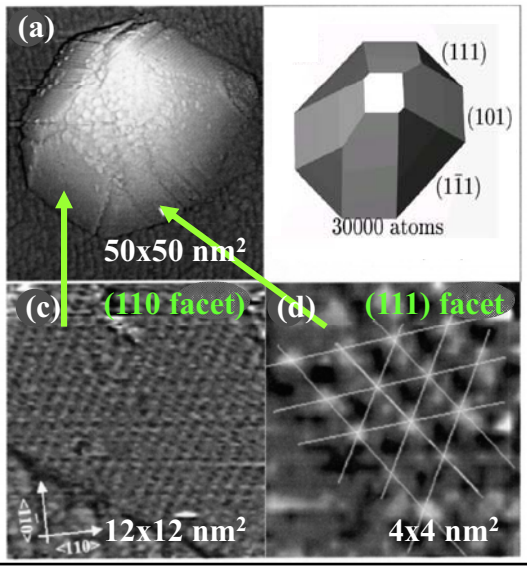
Ga deposition rate
= 0.1 ML/s



Log_{10} of island density does not increase linearly with $1/T$: Unusual *increase* of island density with increasing T (for $T > 800$ K).

InAs/GaAs(001) quantum dots close to thermodynamic equilibrium

G. Costantini et al. APL 82 (2003)



a) STM topography of a large island.

b) Equilibrium shape (theory: ***E. Pehlke, N. Moll, M.S., Proc. 23rd ICPS (1996); Q. Liu, et al., PRB 60 (1999)***).

c), d) High-resolution views of the (110) and (111) side facets.

Also:
J. Marquez et al., APL 78 (2001); Y. Temko et al., APL 83 (2003).

December 10, 2007 in Stockholm

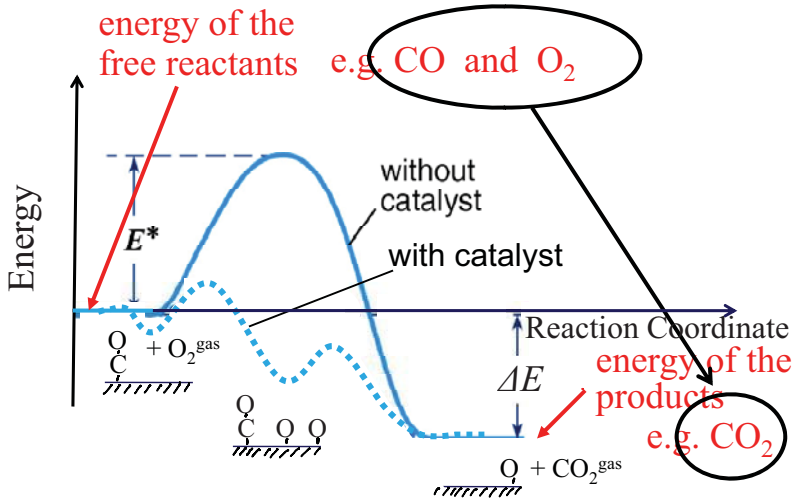
"for his studies of chemical processes on solid surfaces"

Jöns Jakob Berzelius
1779-1848

Wilhelm Ostwald
1853-1932
Nobel Prize in
Chemistry 1909

A catalyst is a substance that accelerates the rate of a chemical reaction without being part of its final product.

Heterogeneous Catalysis

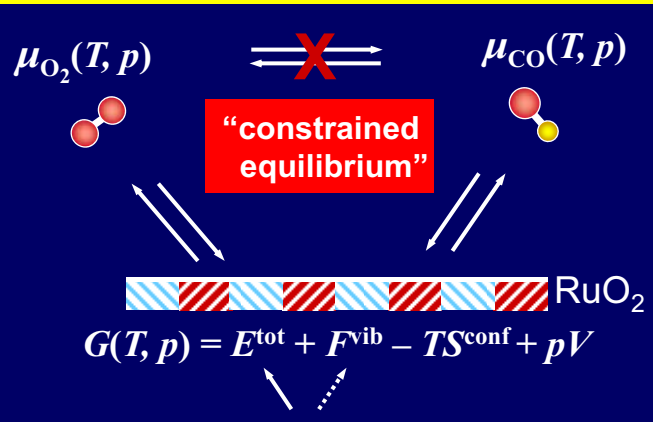


The Steady State of Heterogeneous Catalysis

Points to be addressed:

- We are dealing with is a *thermodynamic open system.*
- A catalyst is a *dynamical* ("living") material. Its *active state* (also called the light-off state) is typically *a novel compound*, created in the realistic environment (atmospheric pressure of various reactive chemicals, high temperatures) during the induction period.
- What's the value of standard concepts such as "the active site" and "the rate limiting step"?

Ab initio atomistic thermodynamics

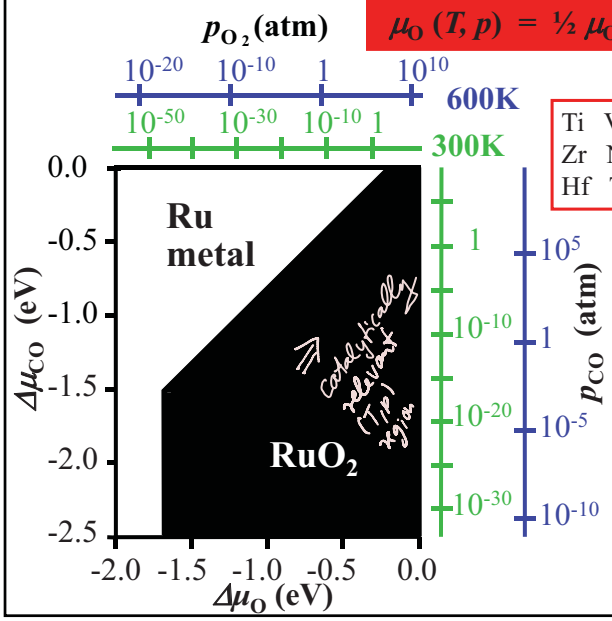


$$\mu_O(T, p) = \tfrac{1}{2}\mu_{O_2}(T, p^0) + \tfrac{1}{2}kT\ln(p/p^0)$$

C.M. Weinert and M.S., Mat. Sci. Forum ***10-12****, 25 (1986).*
Reuter and M. S., PRL ***90****, 046103 (2003).*

Stability of TMs at Catalytic Conditions

$\mu_O(T,p) = \frac{1}{2}\mu_{O_2}(T,p^0) + \frac{1}{2}kT\ln(p/p^0)$

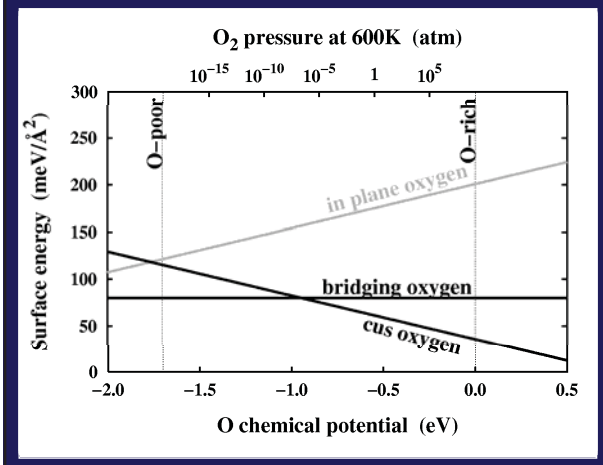


Ti	V	Cr	Mn	Fe	Co	Ni	Cu
Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag
Hf	Ta	W	Re	Os	Ir	Pt	Au

K. Reuter and M. S. Appl. Phys. A 78, 793 (2004)

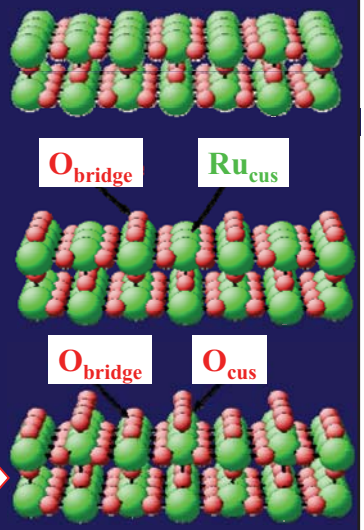
Karsten Reuter

RuO_2(110) surface terminations

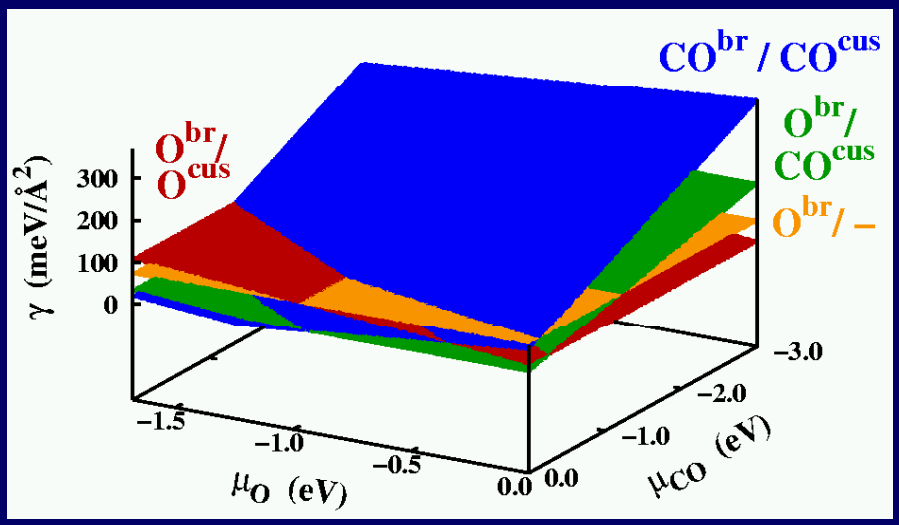


high pressure termination

K. Reuter et al., PRB 65 (2001)

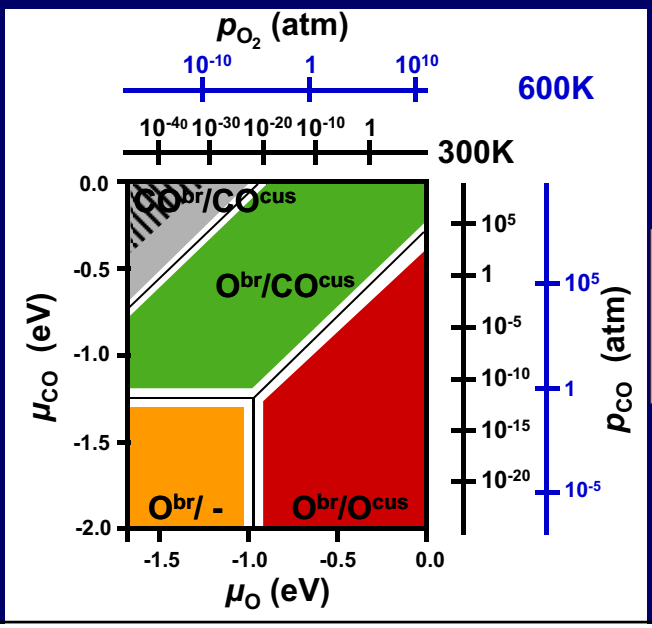


RuO_2 (110) surface structures with O_2 and CO in the gas phase

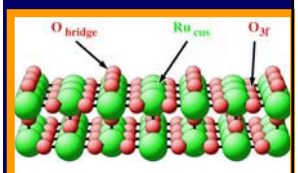


K. Reuter & M.S., PRL 90, 046103 (2003)

RuO_2 (110) stability regions in (*T*,*p*) space



For a "constrained equilibrium"



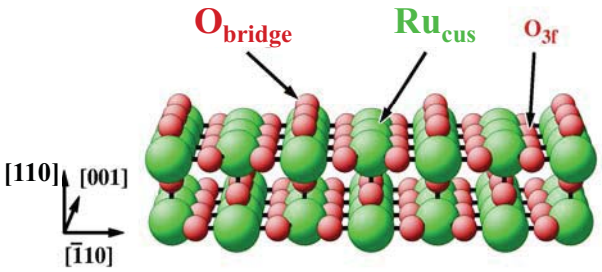
UHV surface termination

K. Reuter & M.S., PRL 90, 046103 (2003)

Surface Composition of RuO_2 (110)

The ***stable surface geometry*** at UHV conditions: There are no vacancies in the O_{bridge} rows.

Confirmed by UHV STM measurements



- In an environment containing O_2 and CO it takes macroscopic time to establish the steady state: ≈ 0.02 s
- The surface composition is noticeably different from any stable or metastable state. It is "somewhat related" to RuO_2 (110) but
  - -- bridge sites are occupied by only ≈90% oxygen atoms.
  - -- Ru_{cus} sites are occupied by ≈70% CO and ≈30% O.

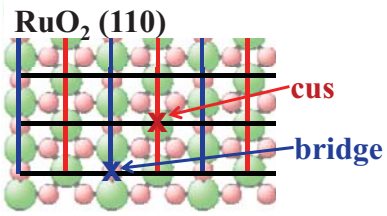
Stat. Mech. of Catalysis from First Principles

example: $CO + ½\ O_2 \rightarrow CO_2$ at RuO_2

1. Analysis of all *possibly relevant* processes using density-functional theory
2. Calculate the rates of all important processes
   $\Gamma^{(i)} = \Gamma_0^{(i)} \exp(-\Delta E^{(i)} / k_B T)$
3. Statistical mechanics approach to describe
   - -- adsorption/desorption of O_2 and CO
   - -- diffusion of O and CO
   - -- surface reactions between
     $CO^{br} + O^{cus}$, $CO^{cus} + O^{cus}$
     $CO^{br} + O^{br}$, $CO^{cus} + O^{br}$

Altogether: 26 processes.

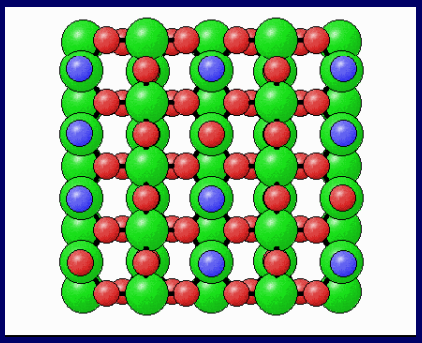
For the general concepts see: Reuter, Stampfl, M.S. in: Handbook of Materials Modeling, ed. by Sidney Yip. Springer, Berlin Heidelberg, 2005.



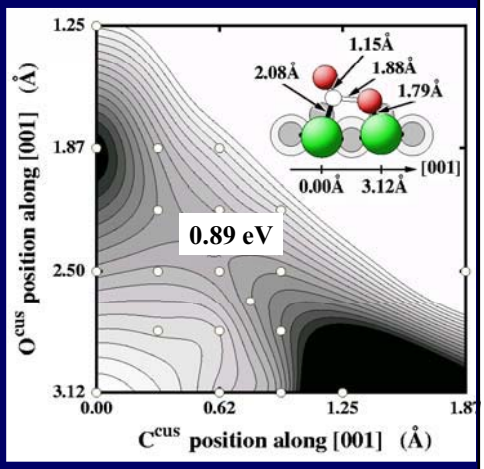
extended kinetic Monte Carlo
(coarse-graining molecular dynamics)

CO_2 Formation Recation; Here the Example

$CO_{cus} + O_{cus} \rightarrow CO_2$

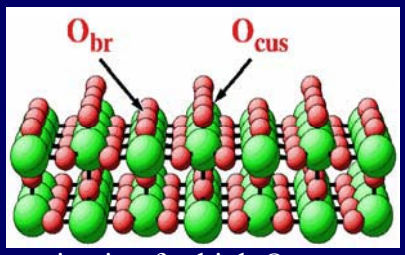


oxygen oxygen of CO

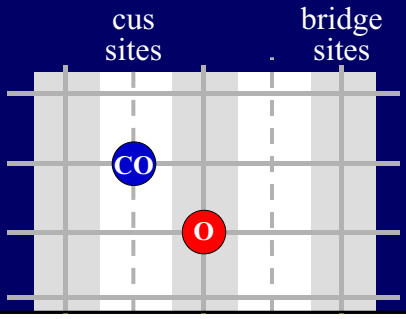


K. Reuter & M.S., PRL ***90****, 046103 (2003) and PRB* ***68****, 045407 (2003).*

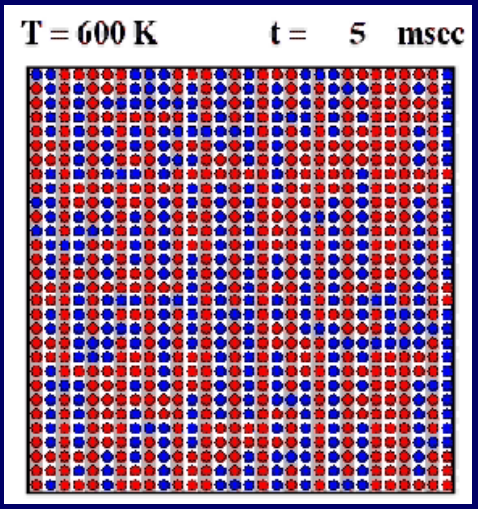
Oxidation catalysis at RuO_2 (110)



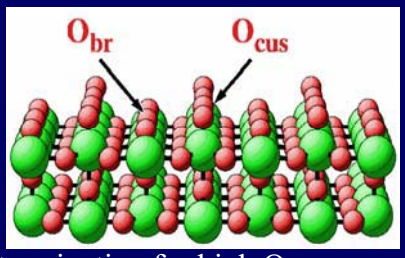
termination for high O_2 pressure



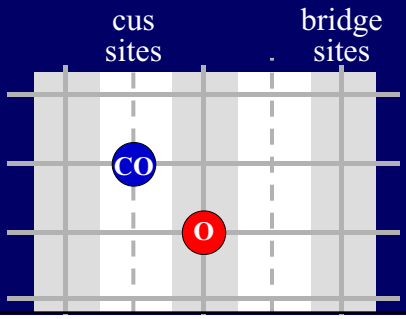
$p(O_2)$ = 1 atm, p(CO) = 10 atm



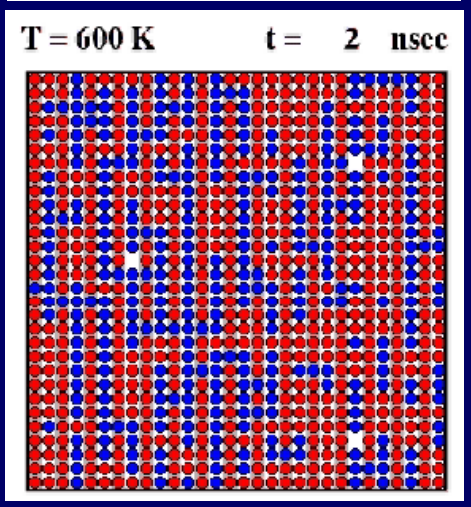
Oxidation catalysis at RuO_2 (110)



termination for high O_2 pressure

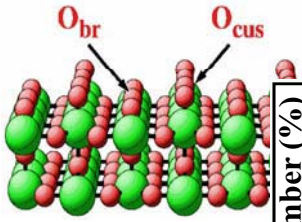


$p(O_2)$ = 1 atm, $p(CO)$ = 10 atm



Site Occupation Statistics at the Steady State (Strong Fluctuations)

K. Reuter, D. Frenkel, M.S., PRL 93, 116105 (2004),
K. Reuter, M.S., PRB 73 (2006).



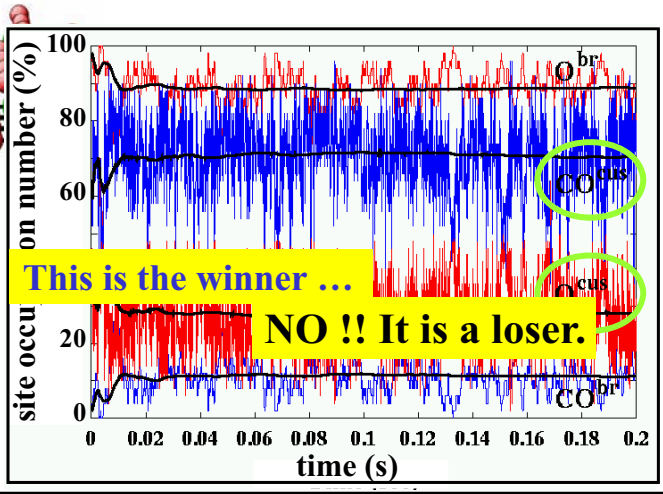
Reaction energy barriers (eV)

$CO^{br} + O^{cus}$: 0.8

$CO^{cus} + O^{cus}$: 0.9

$CO^{cus} + O^{br}$: 1.2

$CO^{br} + O^{br}$: 1.5



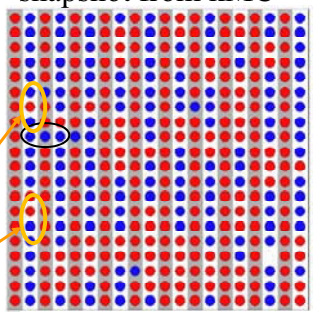
This is the winner …

NO !! It is a loser.

What Kills the Lowest-Energy Process?

The surface structure / composition is not in thermal equilibrium. The kinetics creates a non random structure.

snapshot from kMC



The action is here.

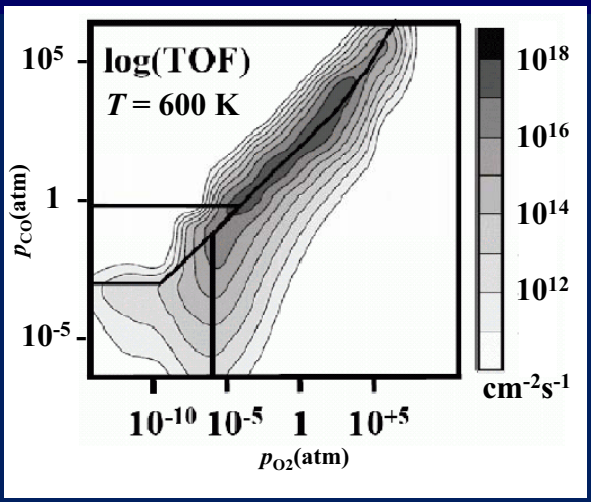
oxygen CO

cus sites: white background
bridge sites: grey background

The $CO^{br} + O^{cus}$ reaction has the lowest energy barrier

*Temel, Meskine, Reuter, Scheffler, and Metiu, J. Chem. Phys. **126**, 204711 (2007)*
Meskine, Matera, Scheffler, Reuter, and Metiu, Surf. Sci. (2009).

RuO_2 (110) High Reactivity Regions
(bridging the pressure gap)



The measured rate is $r_{CO2} = 10^{18}$ cm^{-2} s^{-1}

C.H.F. Peden, D.W. Goodman, D.S. Blair, P.J. Berlowitz, G.B. Fisher, S.H. Oh, J. Phys. Chem. 92 (1988)

K. Reuter, D. Frenkel, M.S., PRL 93, 116105 (2004); K. Reuter, M.S., PRB 73 (2006).

Conclusions

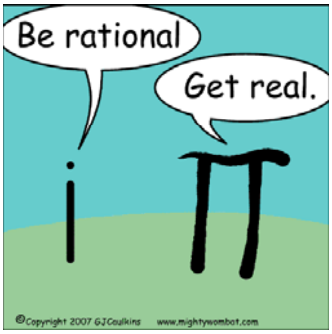
- The described techniques are applicable to a wide variety of gas-phase and solution-phase chemistry, crystal growth, heterogeneous catalysis, etc.
- For the multiscale modeling we need robust, error-controlled links with knowledge of uncertainty between the various simulation methodologies. Some progress has been achieved for DFT → CE → MC and for DFT → MD → kMC.
- However, there are several open questions with respect to the next steps (rate equations, continuum equations, etc.).
- Short time spans (< μs) show interesting MD processes, however, they most likely will miss the important ones.
- Atomistic (and electronic) details actuate and control the function of materials, even at macroscopic lengths and times.

Conclusions: Get Real!

- A material is typically modified significantly under operating conditions (structure and stoichiometry).
- The **"one-structure, one-site, one-mechanism"** description is typically not appropriate.
- Structural instability and fluctuations are important. They enable a high dynamics and healing of (locally) poisoned regions.

We Need

- theory to describe non-adiabatic effects,
- theory to describe heat transport and dissipation, mass transport,
- continue to worry about "strong correlations" and van der Waals interactions,



- more experimental information about the (temporary) formation of the (novel) compounds that form under real-life conditions,
- more experimental information on the role of *fluctuations* and the *correlated* adsorption and reaction *dynamics* at high pressure.