
SPRING COLLEGE ON SCIENCE AT THE NANOSCALE
(24 May - 11 June 2004)

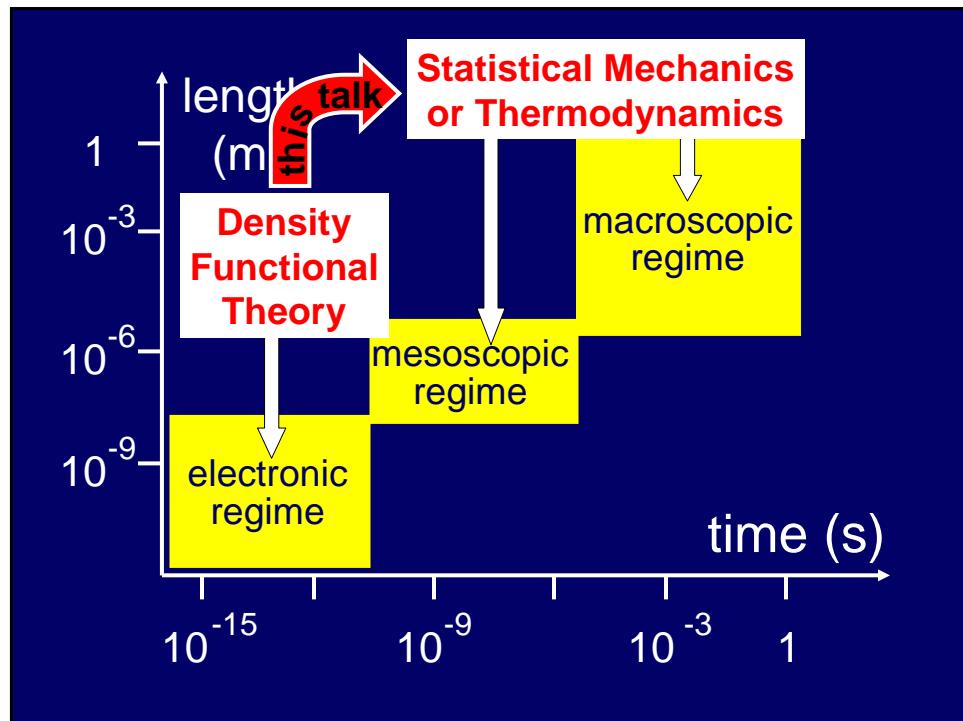
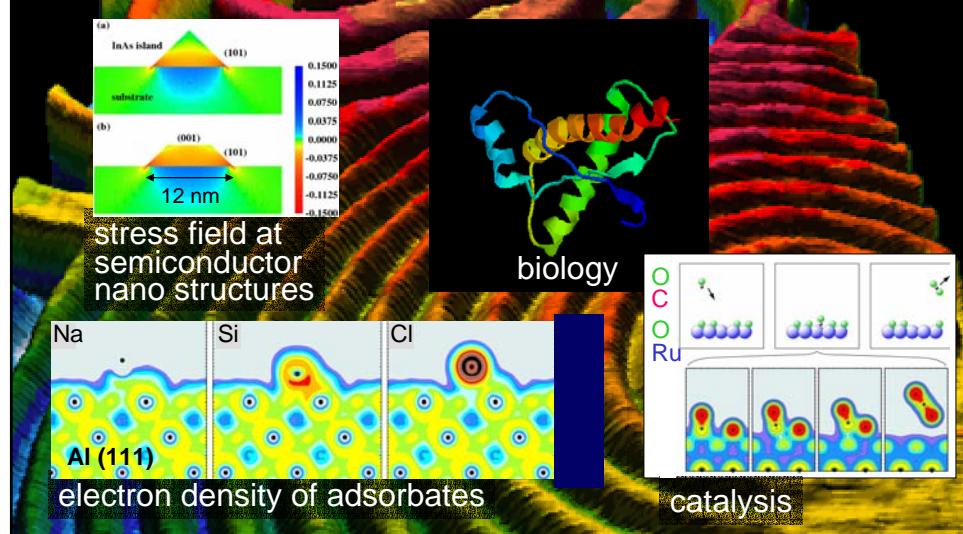
**NANOMETER-SCALE PHYSICS -- THE EXAMPLES OF SEMICONDUCTOR
QUANTUM DOTS AND HETEROGENEOUS CATALYSIS**

Parts I - II - III

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These are preliminary lecture notes, intended only for distribution to participants.

Nanometer-scale physics -- the examples of semiconductor quantum dots and heterogeneous catalysis



Density Functional Theory

The energy of the ground state of a many-electron system : $E_0(\{\mathbf{R}_I\}) = \text{Min}_{\Psi} \langle \Psi | H^e | \Psi \rangle$

Hohenberg and Kohn (1964): The functional

$$n(\mathbf{r}) = n[\Psi] = \langle \Psi | \sum_i \delta(\mathbf{r} - \mathbf{r}_i) | \Psi \rangle$$

can be inverted, i.e.,

$$\Psi(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N) = \Psi[n(\mathbf{r})] .$$

This implies:

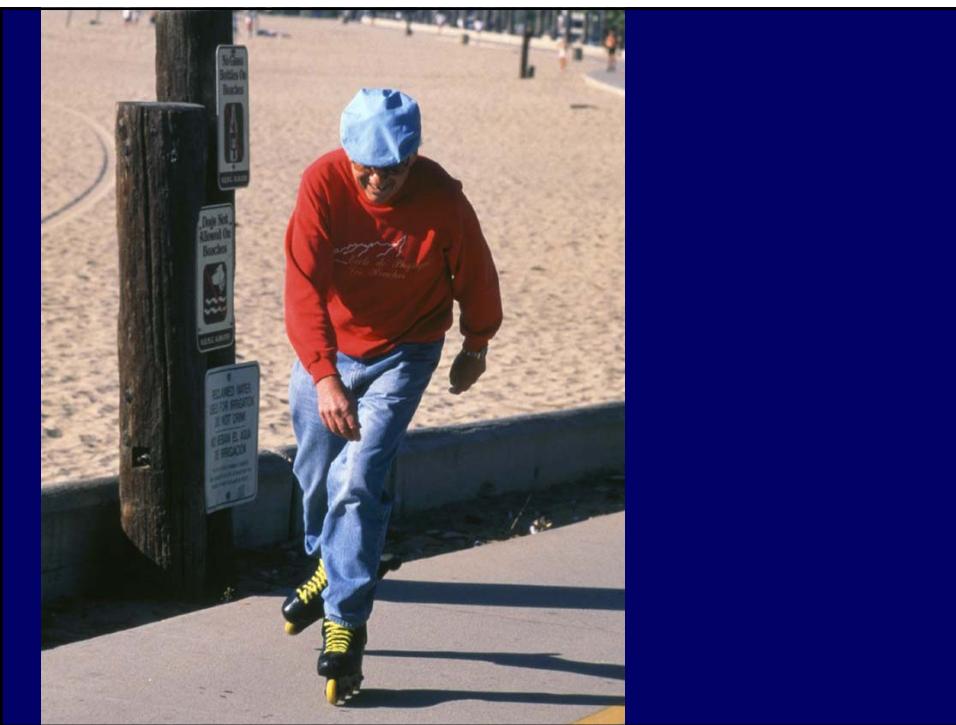
$$E_0(\{\mathbf{R}_I\}) = \text{Min}_{n(\mathbf{r})} E_{\{\mathbf{R}\}}[n]$$

Kohn and Sham (1965):

$$E_{\{\mathbf{R}_I\}}[n] = T_s[n] + \int d^3r v_{\{\mathbf{R}_I\}}^{\text{nuc}}(\mathbf{r})n(\mathbf{r}) \\ + \frac{1}{2} \int \int d^3r d^3r' \frac{n(\mathbf{r})n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} + E^{\text{xc}}[n]$$

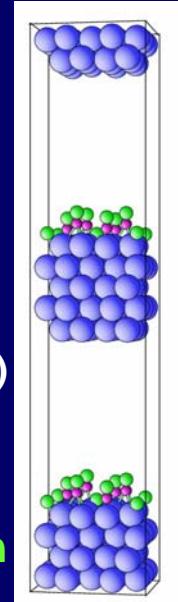
with **local-density approximation**
or **generalized gradient approximation**

Accuracy of geometries is better than 0.1 Å. Accuracy of calculated energies (relative) is better than 0.2 eV [for special cases better than 0.01 eV].

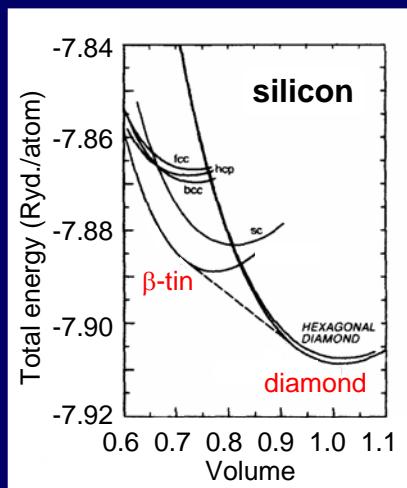


Methods

- I {
- **Density functional theory**
 - ***ab initio* pseudopotentials**
(the fhi98md - code ---
www.fhi-berlin.mpg.de/th/th.html)
 - **FP-LAPW**
(the WIEN - code by
P. Blaha, K. Schwarz, et al.;
M. Petersen et al., CPC **126** (2000))
- II {
- ***ab initio* Molecular Dynamics**
 - ***ab initio* Quantum Dynamics**
 - ***ab initio* Lattice Gas Hamiltonian**
 - ***ab initio* kinetic Monte Carlo**



The First (Convincing) DFT Calculations: Stability of Crystals and Crystal Phase Transitions



M. T. Yin and
M. L. Cohen
PRB **26** (1982)

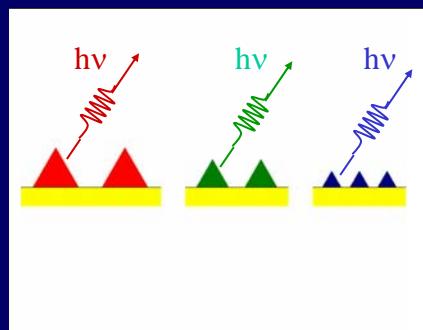
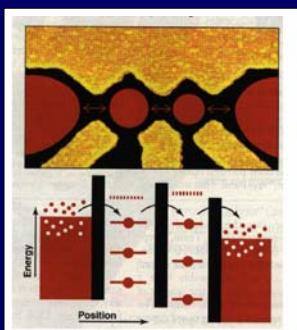
see also:
V.L. Moruzzi, J.F. Janak,
and A. R. Williams
*Calculated Electronic
Properties of Metals*
Pergamon Press (1978)

Self-Assembly of Nano-Scale Structures at Semiconductor Surfaces

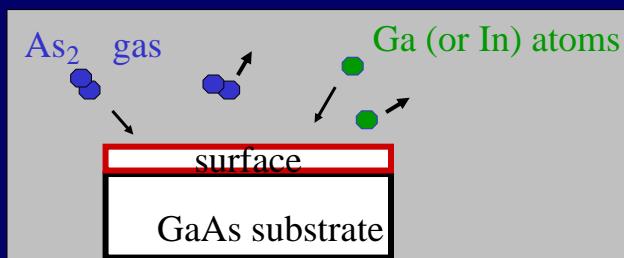
Motivation:

Single-electron transistor

LEDs and
laser diodes

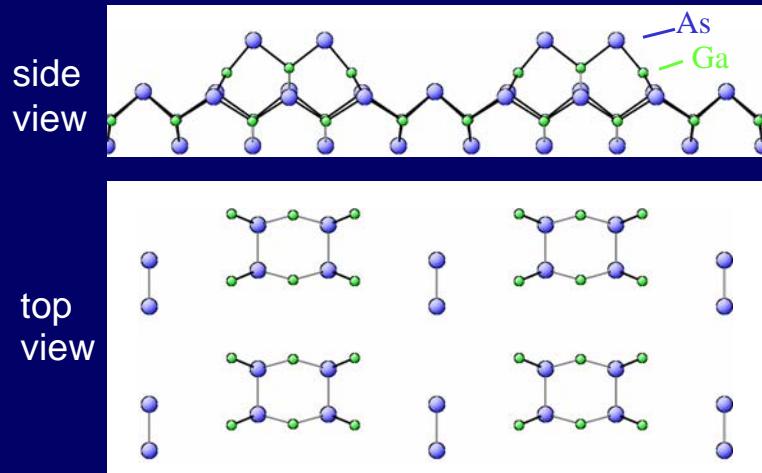


Microscopic processes controlling the growth -- Example: III-V semiconductors



- 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

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

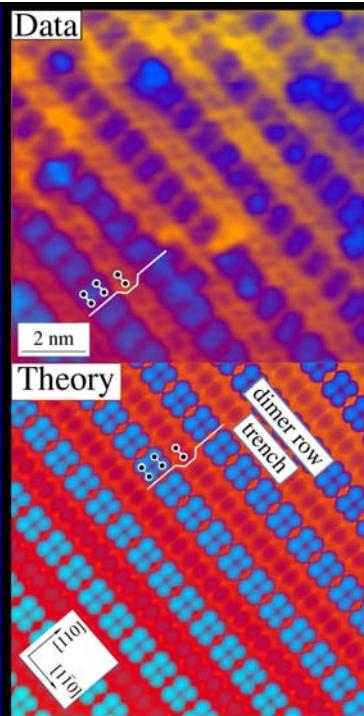


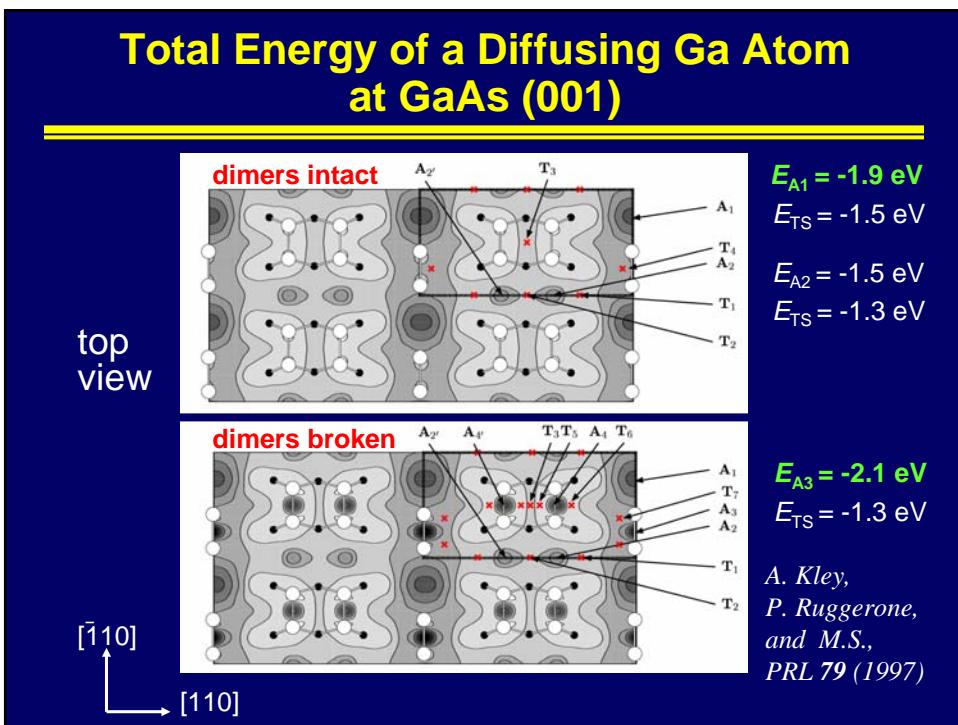
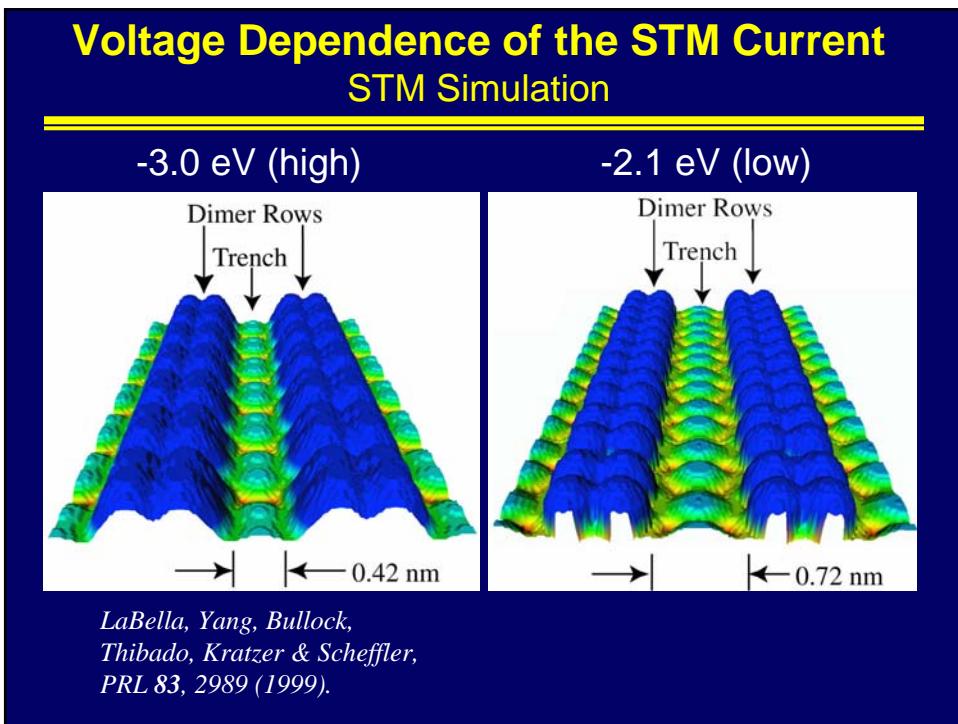
STM Imaging of GaAs(001)

measured filled state image
at $V_{\text{tip}} = -2.1 \text{ eV}$

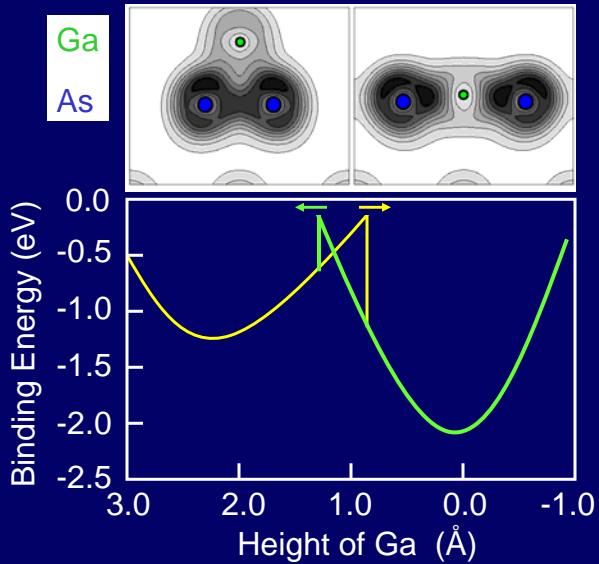
simulated image:
local density of states
integrated to 0.3 eV
below the valence
band maximum

LaBella, Yang, Bullock,
Thibado, Kratzer & Scheffler,
PRL 83, 2989 (1999).





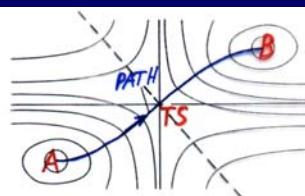
Unusually stable site for Ga adatom inside the trench-site As-dimer



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

P. Kratzer
& M. S.,
to be published

Transition State Theory



Transition state theory

$$\Gamma = \frac{k_B T}{h} \exp\left(\frac{-\Delta F}{k_B T}\right)$$
$$\Delta F = -k_B T \ln Z_{\text{TS}} + k_B T \ln Z_A$$

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

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

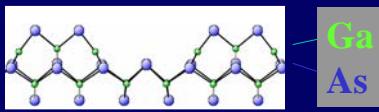
$$\Gamma^{(i)} = \Gamma_0^{(i)} \exp(-\Delta E^{(i)} / k_B T)$$

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

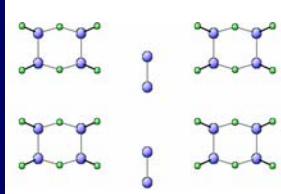
→ kinetic Monte Carlo method

Adsorption, diffusion, island nucleation, and growth of GaAs

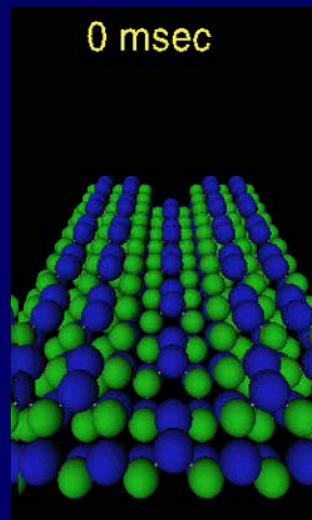
side view



top view



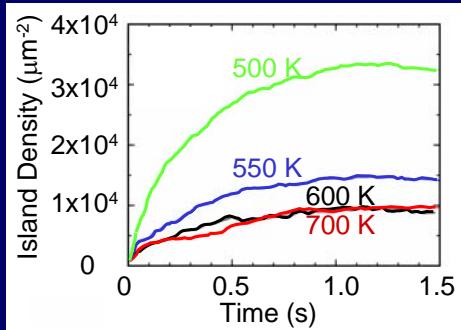
1/60 of the full simulation cell
As₂ pressure ≈ 1.33 × 10⁻⁸ bar
Ga deposition rate = 0.1 ML/s
T = 700 K



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

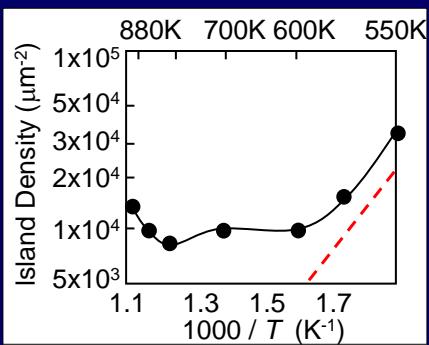
Island density

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



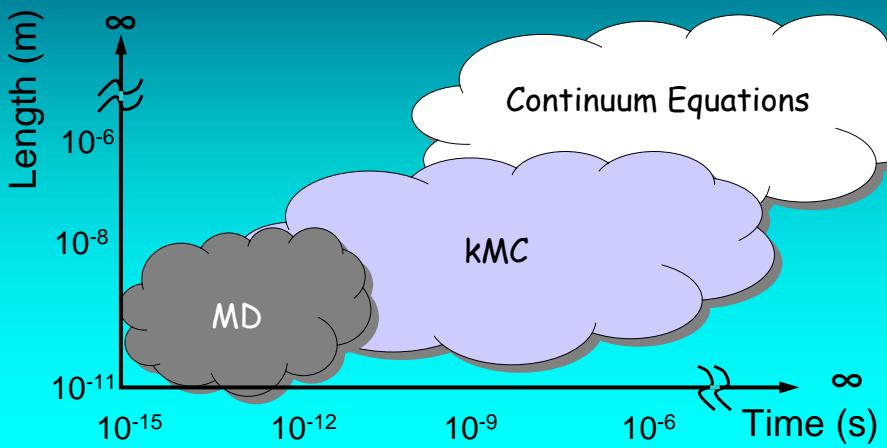
As₂ pressure
= 1.33×10^{-8} bar

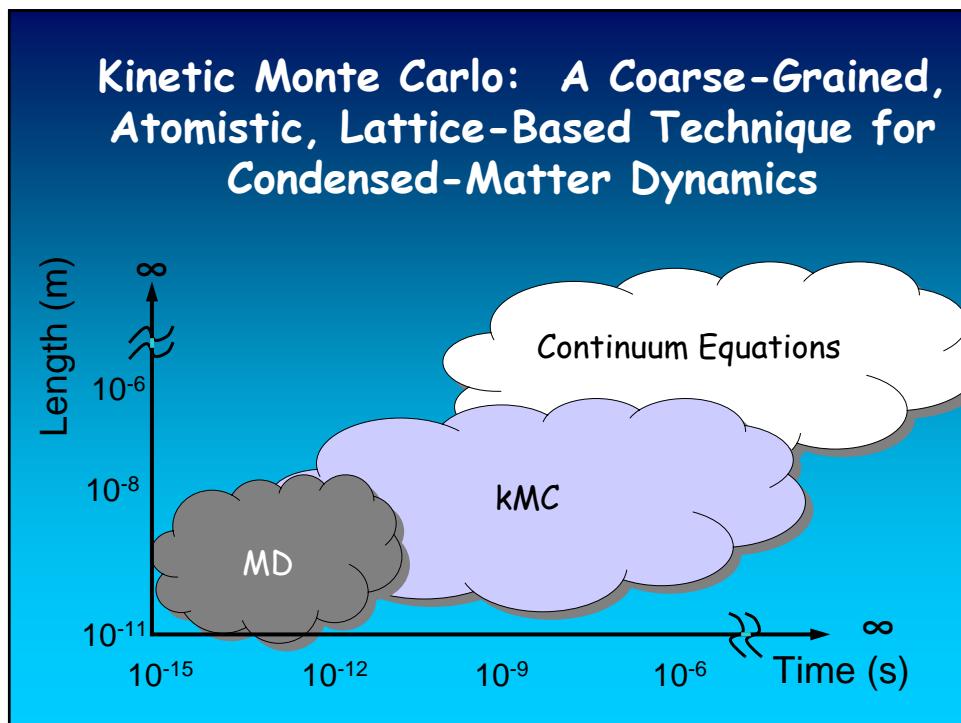
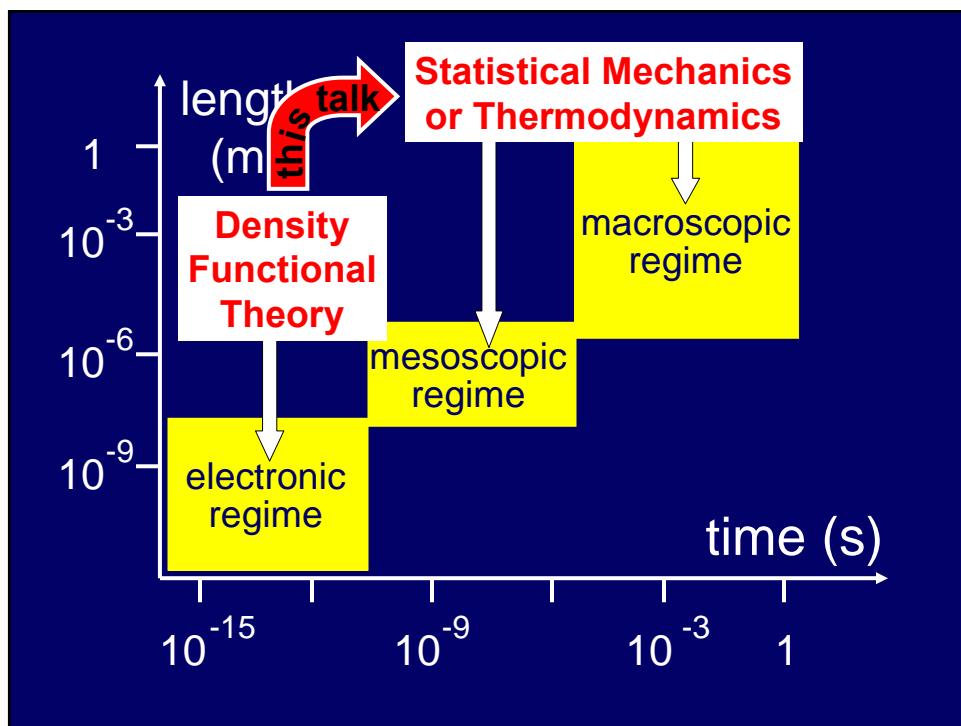
Ga deposition rate
= 0.1 ML/s



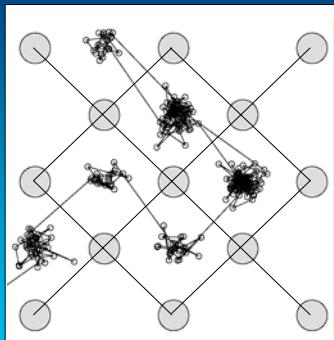
\log_{10} of island density does not increase linearly with $1/T$: Unusual *increase* of island density with increasing T (for $T > 800$ K).

Kinetic Monte Carlo: A Coarse-Grained, Atomistic, Lattice-Based Technique for Condensed-Matter Dynamics

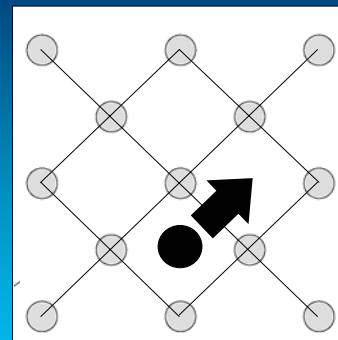




Kinetic Monte Carlo: Coarse-Graining MD



MD of Co on Cu(001):
The Whole Trajectory



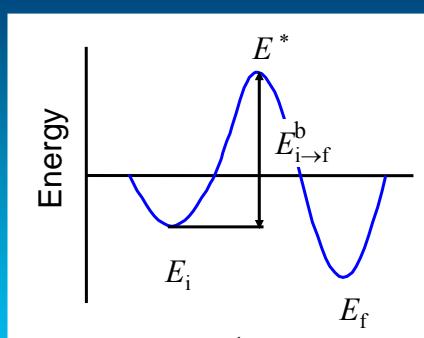
KMC: Coarse-Grained
Hops

KMC Transition Probabilities and the Detailed-Balance Criterion

$$\frac{W(\vec{x} \rightarrow \vec{x}')}{W(\vec{x}' \rightarrow \vec{x})} = \exp[-\delta A/k_B T]$$

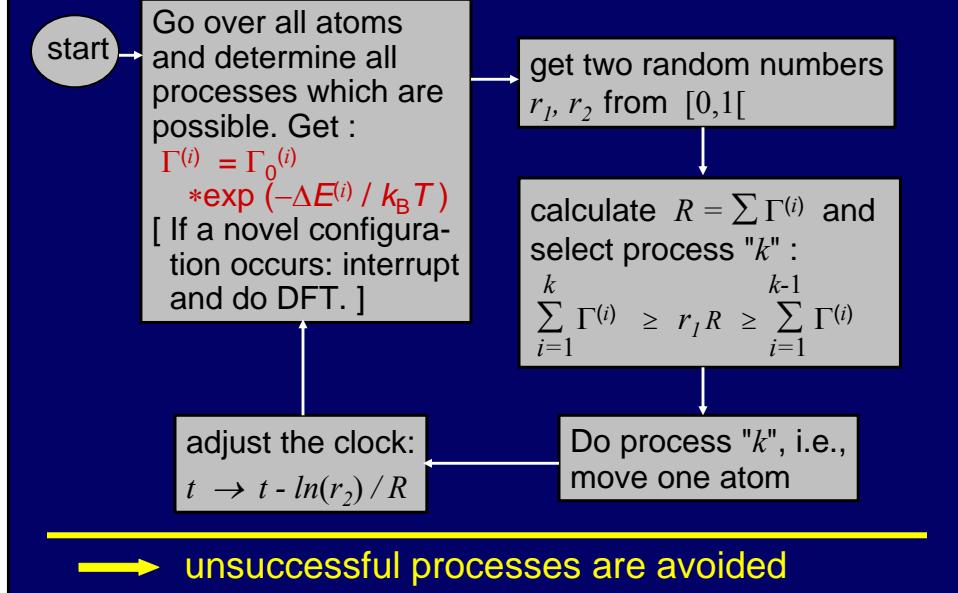
Metropolis MC Satisfies Detailed Balance, but not Kinetics

$$W(i \rightarrow f) = \begin{cases} 1 & \text{if } E_f \leq E_i \\ e^{-\Delta E/k_B T} & \text{if } E_f > E_i \end{cases}$$

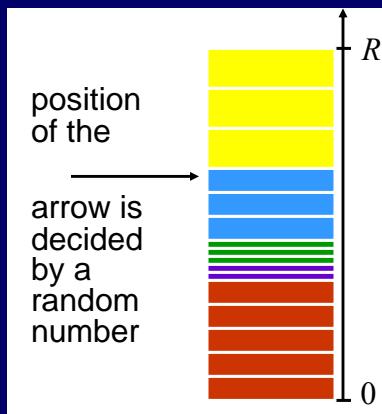


TST Satisfies Detailed Balance and Kinetics

Flowchart of kinetic Monte Carlo Simulation



Sketch of the kMC Approach

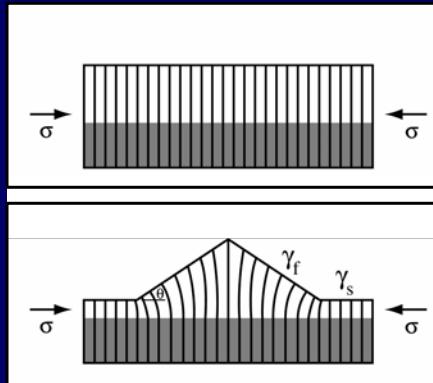


Graphical sketch of the statistics of the process that will be chosen in the kMC approach. Each bar corresponds to a certain atom. The color refers to the type of process, and the thickness to the rate.

for example:

- yellow:** Ga diffusion in the trench;
- light blue:** Ga diffusion perpendicular to trench;
- green:** Ga enters an As dimer;
- dark blue:** Ga diffusion parallel to steps;
- red:** As₂ adsorption into the intermediate.

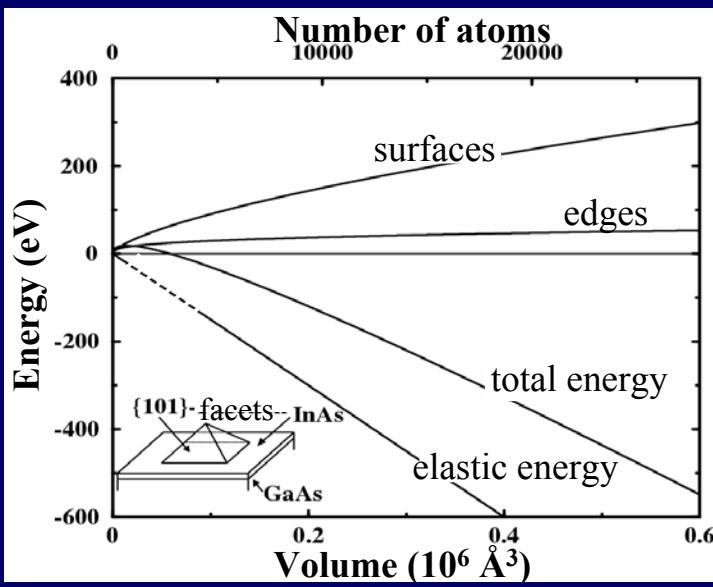
Stranski-Krastanow morphology as one way to reduce misfit strain energy



e.g.
InAs on
GaAs

For InAs/GaAs the SK model describes
only a part of the full picture

Equilibrium Shape of Quantum Dots

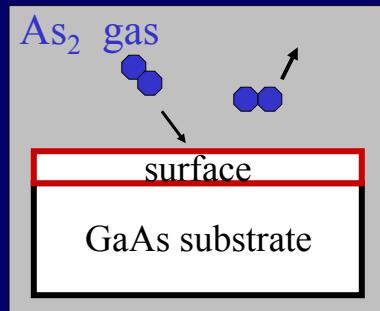


L. Wang,
P. Kratzer,
and M.S.,
PRL 82
(1999)

Stoichiometry and Structure of the Surface depend on the Environment

(atomic chemical potentials)

$$E_{\text{surface}} = \Delta E_{\text{tot}} - N_{\text{Ga}} \mu_{\text{Ga}} - N_{\text{As}} \mu_{\text{As}}$$



$$\mu_{\text{Ga}} + \mu_{\text{As}} = E^{\text{bulk}}(\text{GaAs})$$

Only one independent variable:

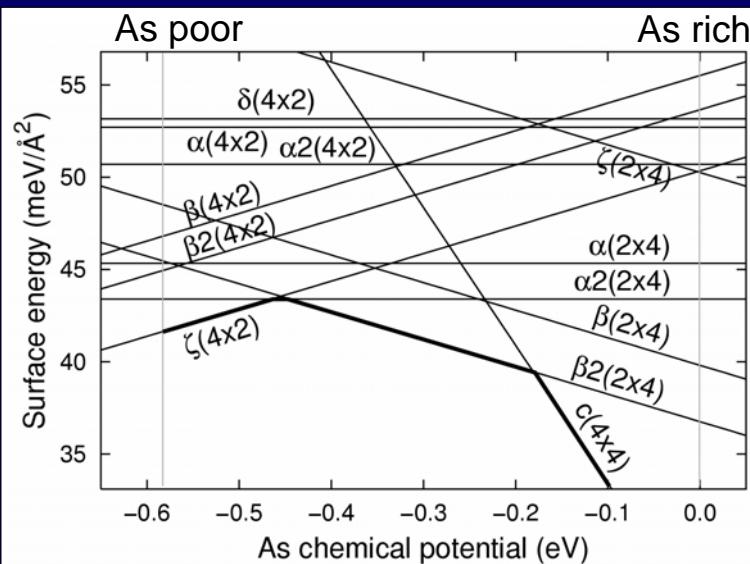
$$\mu_{\text{As}}(T, p) = \frac{1}{2} \mu_{\text{As}_2}(T, p^0) + \frac{1}{2} kT \ln(p/p^0)$$

ab initio atomistic thermodynamics

C.M. Weinert and M.S., Mat. Sci. Forum 10-12, 25 (1986).

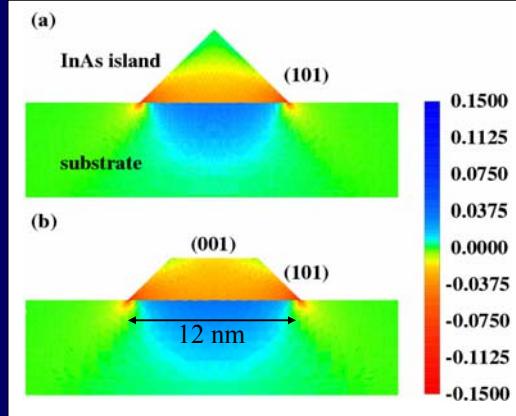
Reuter and M. S., Phys. Rev. B 65, 035406 (2002); PRL 90, 046103 (2003).

Surface Energies of Clean GaAs (001)

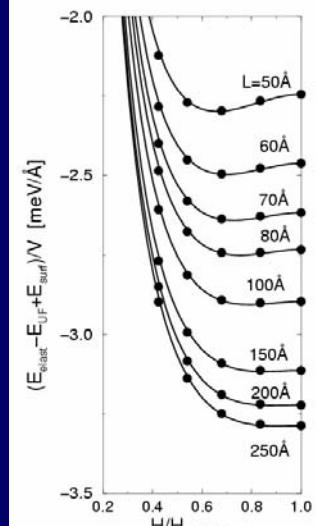


Sung-Hoon Lee, W. Moritz, & M.S., PRL 85, 3890 (2000)

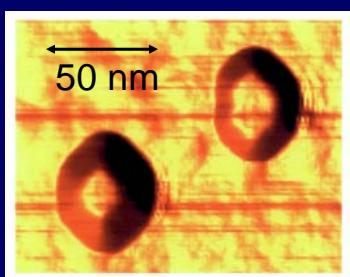
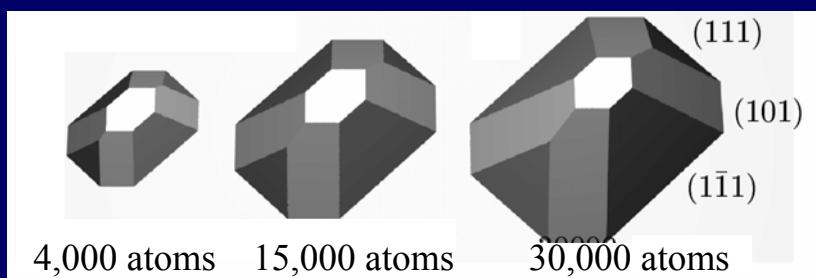
Stress Tensor at strained InAs Islands on GaAs



N. Moll, M.S., and E. Pehlke,
PRB **58**, 4566 (1998)



InP Quantum Dots on GaP(001)

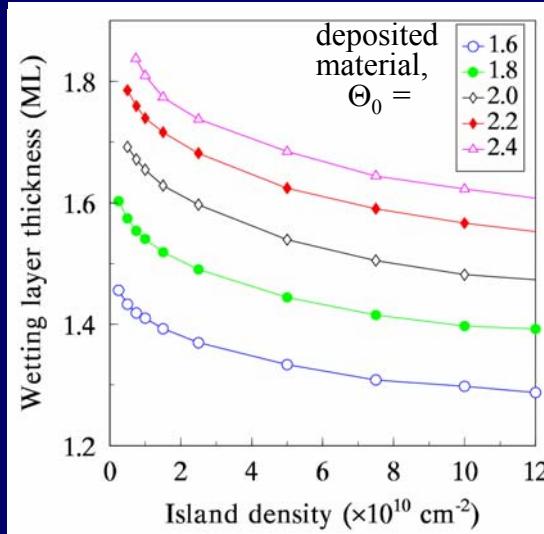


Q. Liu, E. Pehlke,
N. Moll, and M.S.,
PRB **60** (1999)

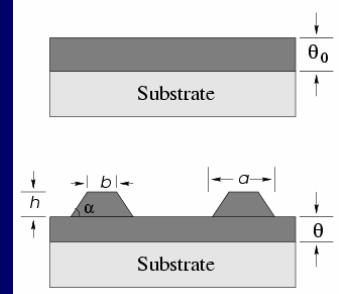
InP islands on GaInP
grown by MOVPE

Samuelson et al. (1996)

Thickness of the Wetting Layer Depends on the Island Density

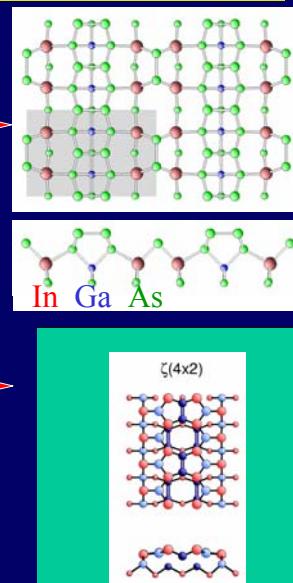
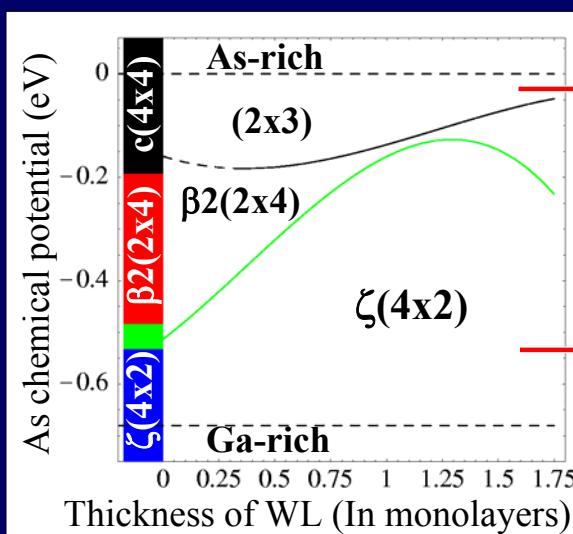


InAs on GaAs
 $\mu_{\text{As}} = E^{\text{bulk}}(\text{As}) - 0.2 \text{ eV}$



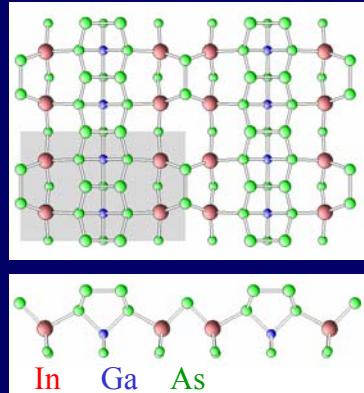
L. Wang, P. Kratzer,
& M.S., PRL 82 (1999)

Reconstruction of the Wetting Layer



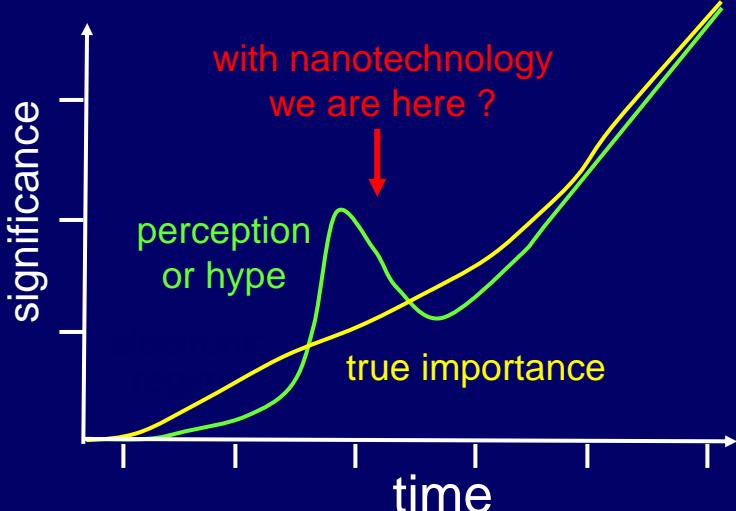
Small islands grow fast, and big (coherent) quantum dots develop a "repulsive ring"

- The wetting layer is an InGaAs **surface alloy** [(2x3) reconstruction] and provides faster diffusion.
- Close to quantum dots the (2x3) structure becomes unstable.



E. Penev, P. Kratzer, & M.S., submitted (2002)

Emerging new technologies



Commercial Process of Styrene Production

Dehydrogenation of

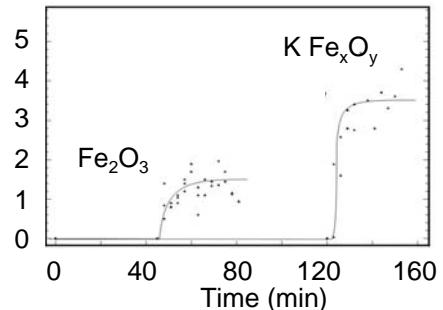
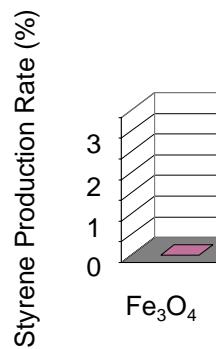
Ethylbenzene to Styrene



Parameters of the commercial process:

- reaction temperature: 580-640°C
- pressure: atmospheric
- component of feed gas: $\text{H}_2\text{O} / \text{EB} = 6 / 9$
- selectivity to styrene: 95%

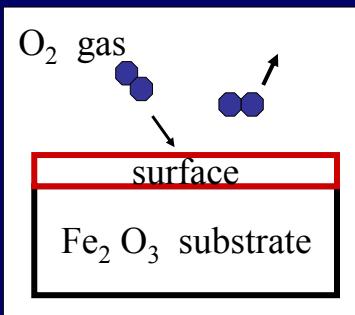
Catalytic Activity



Stoichiometry and Structure of the Surface depend on the Environment

(atomic chemical potentials)

$$\gamma_0(T, p) A_0 = E_{\text{total}} - N_O \mu_O - N_{\text{Fe}} \mu_{\text{Fe}}$$



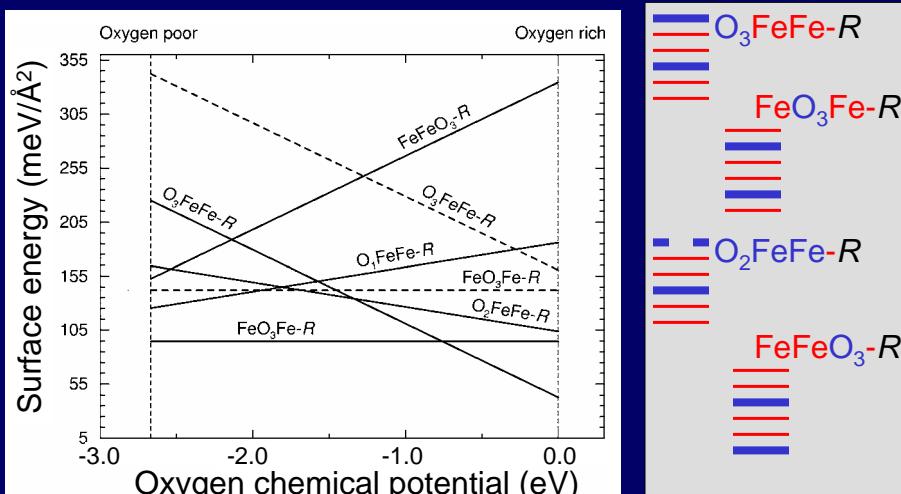
$$2 \mu_{\text{Fe}} + 3 \mu_O = E^{\text{bulk}}(\text{Fe}_2\text{O}_3)$$

Only one independent variable:

$$\begin{aligned} \mu_O(T, p) &= \\ &= \frac{1}{2} \mu_{\text{O}_2}(T, p^0) + \frac{1}{2} kT \ln(p/p^0) \end{aligned}$$

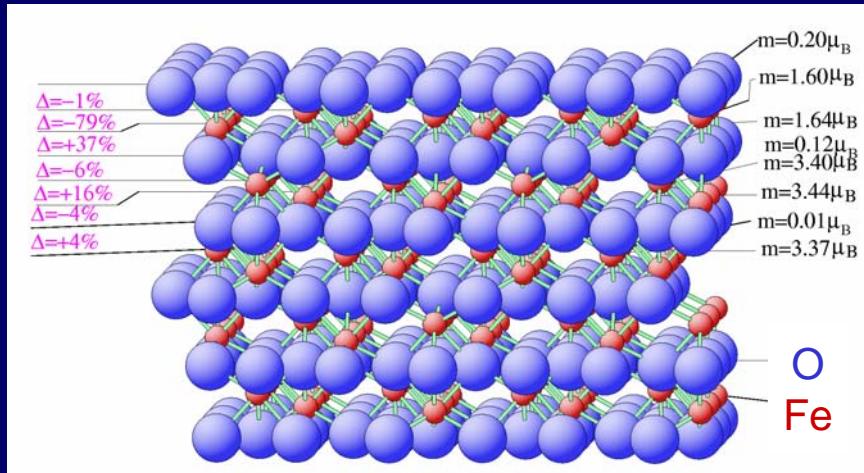
ab initio atomistic thermodynamics

Fe_2O_3 (0001) Surface Terminations



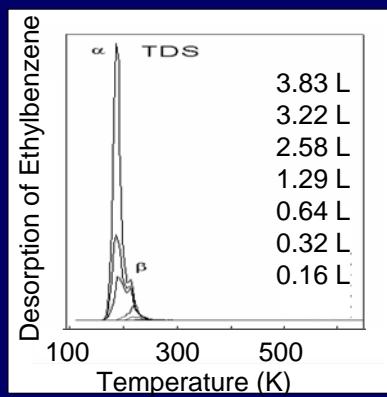
X.G. Wang et al., PRL 81 (1998)

Fe₂O₃ (0001) O-terminated Surface



X.G. Wang *et al.*, PRL 81 (1998)

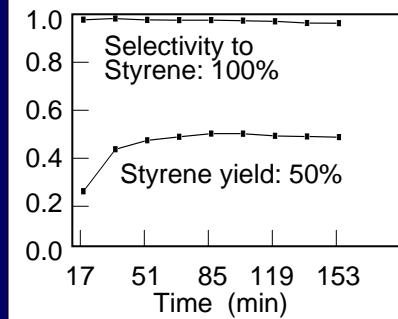
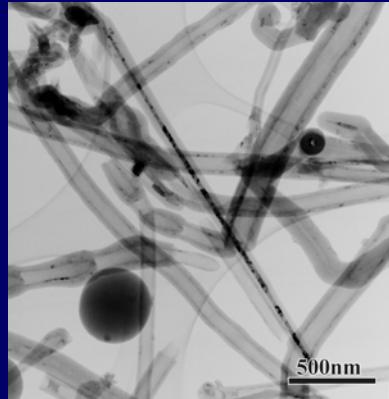
What is the active catalyst ?



- The surface is fully covered with carbon (and oxygen)
- Ethylbenzene does not interact with iron oxide
- How is the production of styrene is catalyzed by iron oxide ?

C. Kuhrs and R. Schlögl,
to be published

Carbon Nanotubes for EB Conversion



R. Schlögl et al., to be published

Reaction temperature

450°C

Concentration of
ethylbenzene in the stream

$1 \cdot 10^{-5}$ mol/ml

Flow of the stream

10 ml/min

Some conclusions on the ab initio atomistic thermodynamics approach

- The described techniques are applicable to a wide variety of gas-phase and solution-phase chemistry, crystal growth, self-assembly, self-organization, heterogeneous catalysis, etc.
- The active phase present under realistic conditions is not the bulk phase introduced as “the catalyst”, but a different (sometimes novel) material with different composition and different structure. Recent examples include: hematite, Ru, Rh, Pd, Ag.

Where do we stand with the first-principles description of materials?

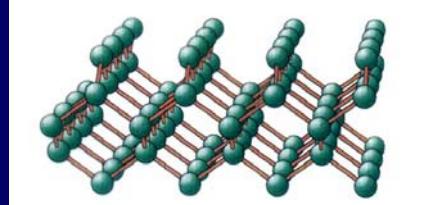
- Properties that are given by ensemble averages or ruled by the statistical interplay of many processes are well described by DFT-GGA.
- Errors in total energies can be noticeable. Even for energy differences they can be as large as several tenths of an eV. And sometimes this is indeed crucial.

Sometimes we need to do better than DFT-GGA!!

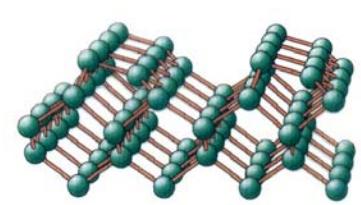
**Improving the accuracy of the xc energy
(exploiting the nearsightedness)
-- local correction of the xc energy --**

Example: surface structure and surface chemical reactions at Si(001)

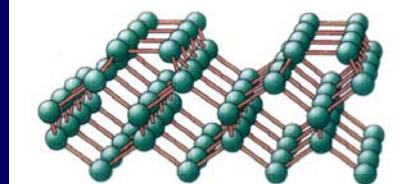
Dimerization and dimer buckling at Si(001)



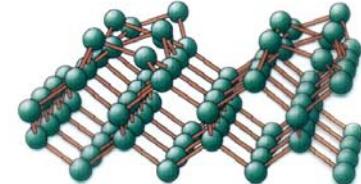
truncated bulk geometry



dimer buckling



formation of dimers

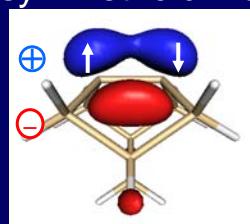


alternating buckling

Buckling at the clean Si(001) surface is sensitive to electron correlation and electron-lattice coupling

"A negative U system" ?

HOMO of symmetric dimer

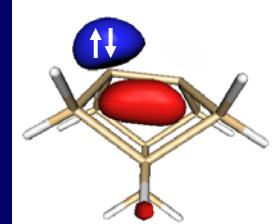


favored by MCSCF (clusters)

Which configuration is the ground state ?

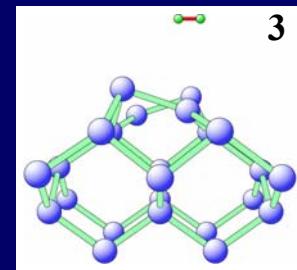
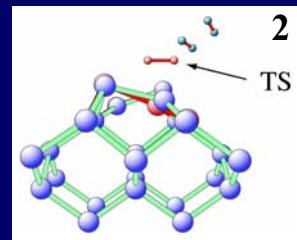
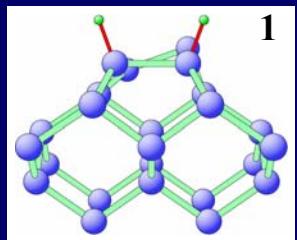
this one

HOMO of buckled dimer



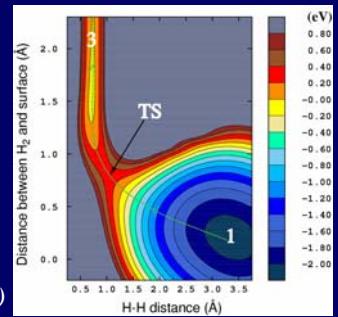
favored by DFT (slabs)

The H₂ / Si(001) energy barrier puzzle

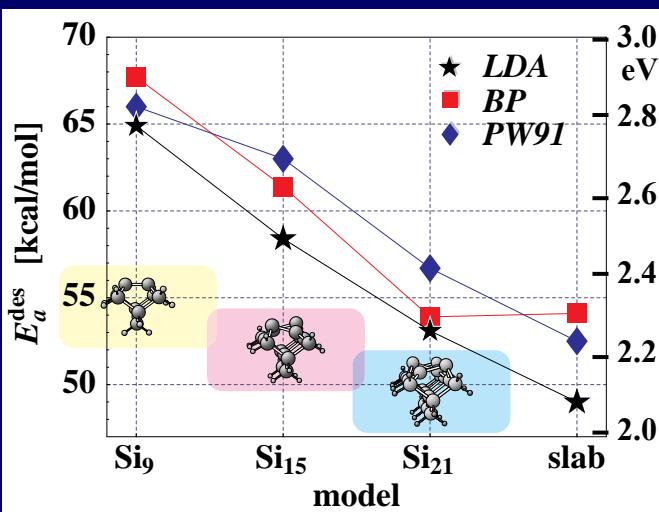


- CI-cluster and DFT-slab calculations give very different descriptions.
- Neither of them agrees with experiment.

A. Gross, M. Bockstedte,
and M.S., PRL 79 (1997)



Cluster models: H₂ dissociative adsorption



Convergence
with cluster
size is slow.

E. Penev, P. Kratzer,
and M. Scheffler,
J. Chem. Phys. 110,
3986 (1999)

Exploiting the Nearsightedness

- DFT-GGA super-cell calculations
- Cluster calculations with DFT-GGA and with QMC
- Correction of the DFT-GGA exchange-correlation energy:
 $\Delta E = E_{\text{cluster}}(\text{QMC}) - E_{\text{cluster}}(\text{GGA})$

*C. Filippi, S.B. Healy,
P. Kratzer, E. Pehlke, M. S.,
PRL 89, 166102 (2002).*

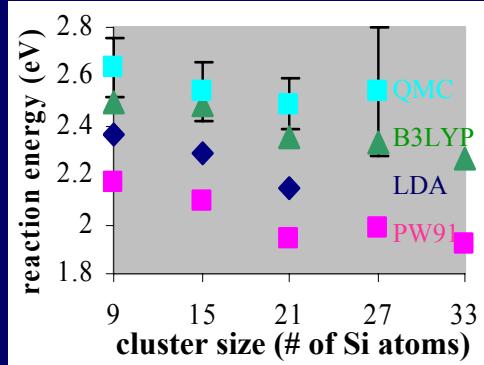
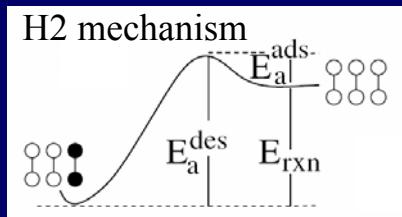
cluster geometries from
DFT-GGA + super-cell

HF MCSCF

Variational QMC
iterative improvement of
Jastrow factor

Diffusion QMC
(starting from VMC
trial wave function)

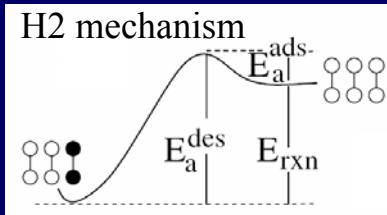
Correction of the xc Energy



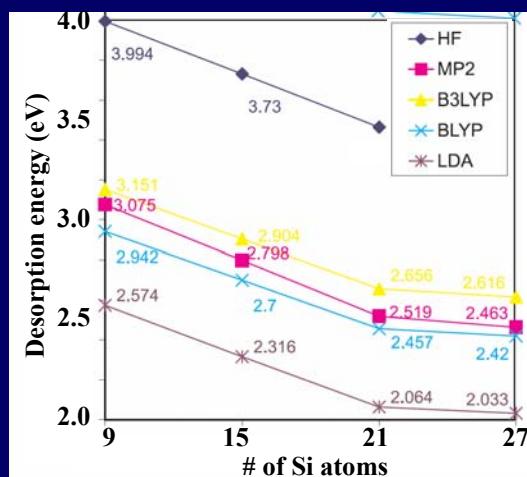
$$\Delta E = E_{\text{cluster}}(\text{QMC}) - E_{\text{cluster}}(\text{GGA}) = 0.48 \pm 0.1 \text{ eV}$$

C. Filippi, S.B. Healy, P. Kratzer, E. Pehlke, and M. S., PRL 89, 166102 (2002).

Checking the quality of the xc treatment



- The total energy is nearsighted, but not much:
Convergence with cluster size is slow.
- $\Delta E = E^{\text{WF}} - E^{\text{DFT-LDA}}$ is very nearsighted.



Is the *direct* DFT route too complicated?

- The xc energy, E_{xc} , stems from many-body theory.
- E_{xc} is a functional of the density, but maybe impossible to handle as such. Maybe, for the accuracy we need, we have to use a "detour" (we do so already for $T_s[n]$).

➡ Calculate a correction to $E_{\text{xc}}^{\text{A}}[n]$ from the many-body wave function Ψ_0 .

We are not giving up DFT !

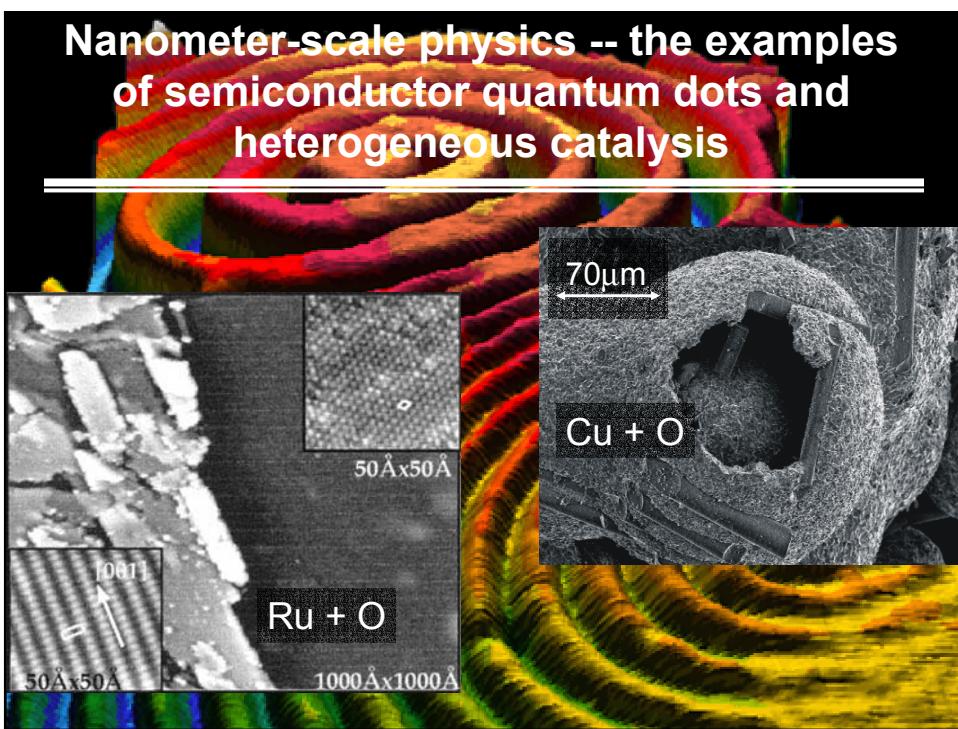
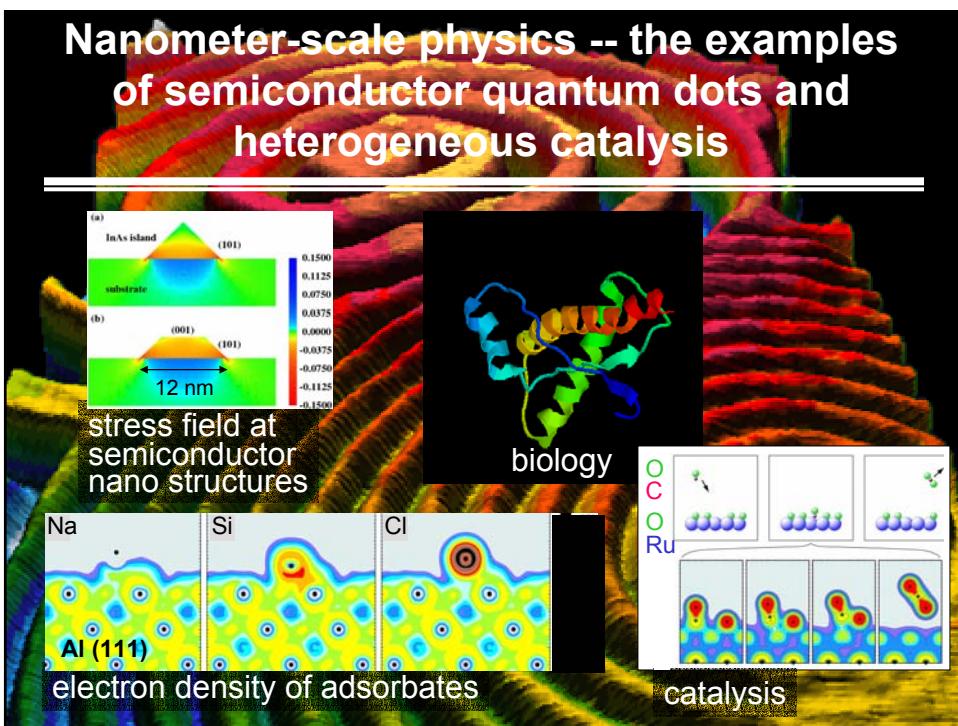
DFT together with tractable xc functionals gives a blurred, sometimes distorted description of reality this is good and helpful !

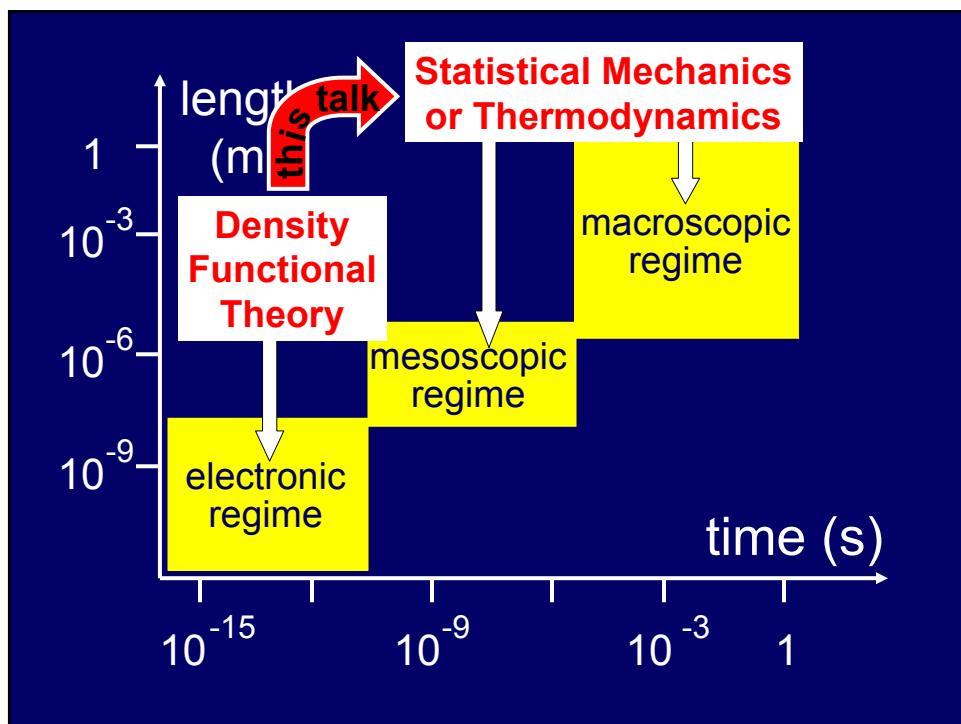
Sometimes corrections are necessary. The xc energy, E_{xc} , is a functional of the density, but maybe impossible to handle as such. Maybe, for the accuracy we need, we have to use a "detour" (we already do so for $T_s[n]$).

The many-body wave function, Ψ_0 , is a functional of the density, as is the many-body Hamiltonian.

Conclusions

- Combining DFT and Statistical Mechanics or Thermodynamics is essential for understanding the function of materials.
- The accuracy of the method is (even) better than its reputation (compensation of DFT-LDA/GGA errors due to the statistical interplay of many processes).
- The described techniques are applicable to a wide variety of gas-phase and solution-phase chemistry, surface phase transitions, crystal growth, heterogeneous catalysis, etc.
- Nearsightedness enables us to correct E^{xc} :
$$\Delta E^{xc} = E_{\text{cluster}}^{\text{WF}} - E_{\text{cluster}}^{\text{DFT-LDA}}$$

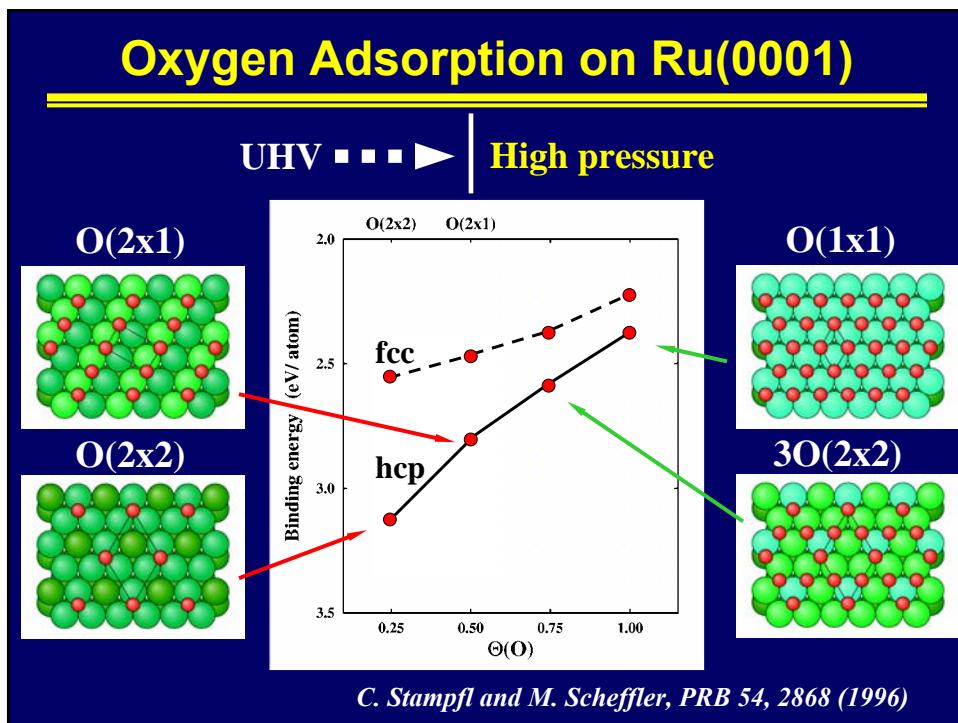
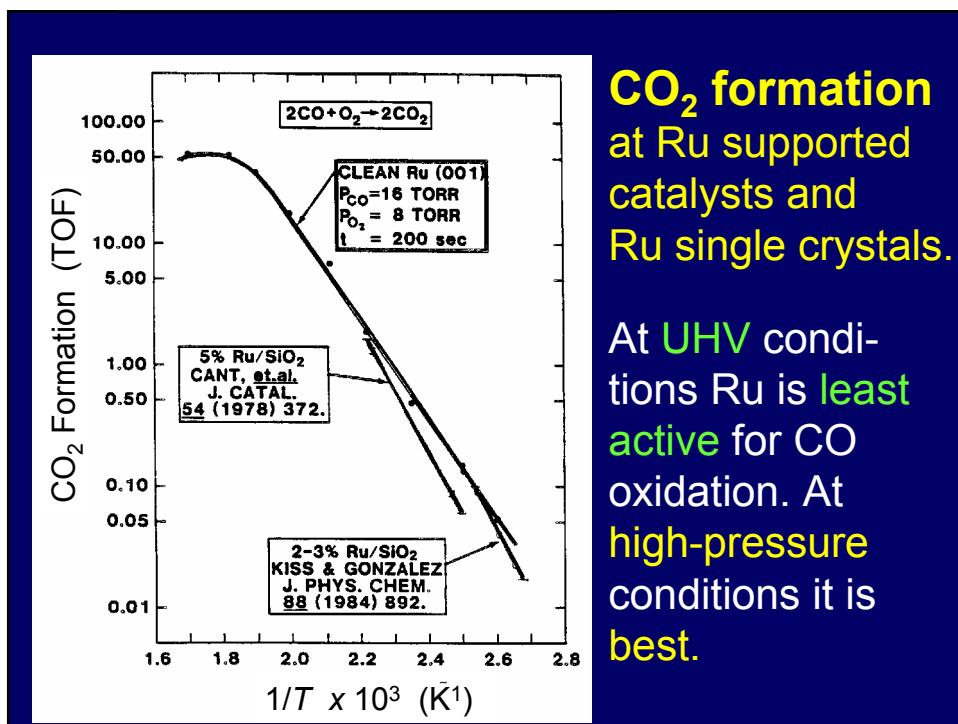




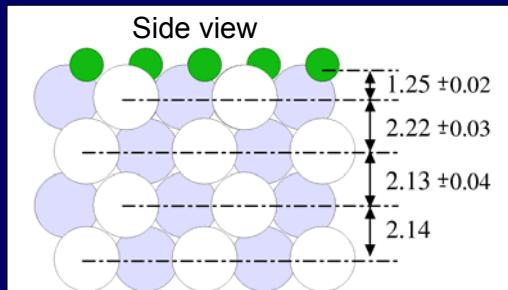
Oxidation catalysis, e.g.:



A "simple", prototypical surface chemical reaction



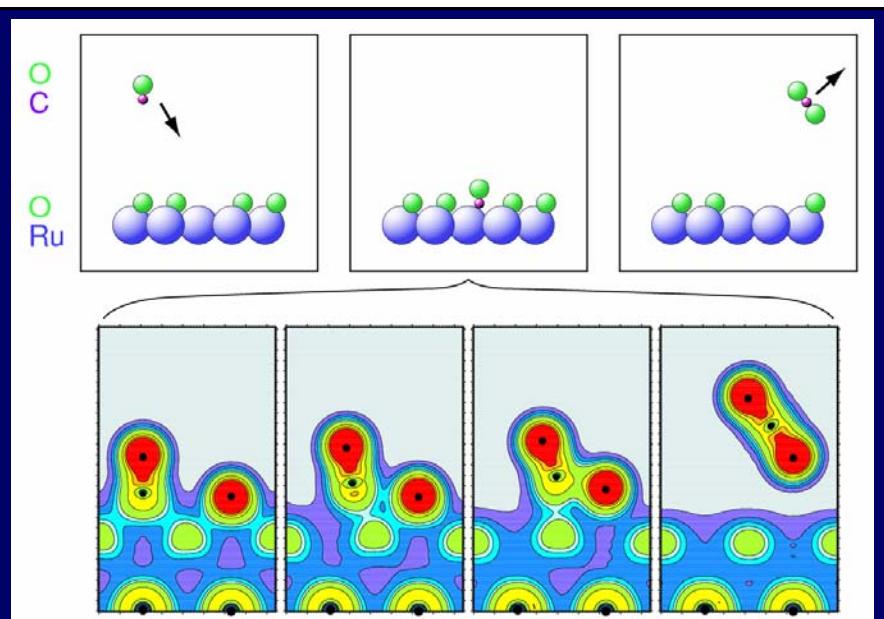
Prediction of new (unexpected) structures. Example: (1x1)-O/Ru(0001)



Prepared by O₂ adsorption up to 1/2ML, (2x1) phase, then NO₂ exposure at 600K to form 1ML (1x1) phase.

PARAMETER	DFT-GGA	LEED
Ru-O spacing (Å)	1.26	1.25 ± 0.02
Ru-O bond length (Å)	2.03	2.00 ± 0.03
Ru-Ru ₂ spacing (%)	+2.7	+3.7 ± 1.4
Ru ₂ -Ru ₃ spacing (%)	-0.9	-0.5 ± 1.8

C. Stampfl et al., PRL 77 (1996)

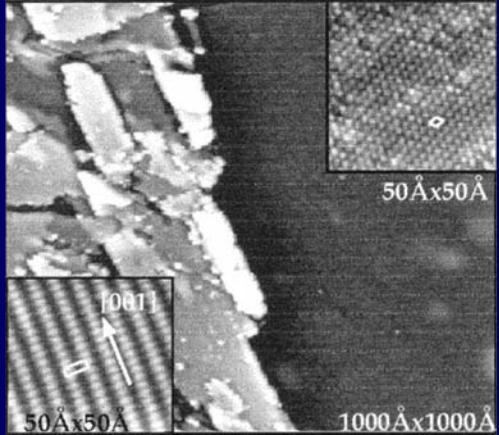


C. Stampfl, M. Scheffler, Surf. Sci. 433-435, 119 (1999),
M. Scheffler and C. Stampfl, in Handbook of Surface Science (2000)

Transition-metals~~s~~ oxides as oxidation catalysts ? !

Catalytic activity of Ru(0001) is due to RuO₂(110) domains (1-2 nm thin films), that form in the reactive environment.

H. Over, Y.D. Kim, A.P. Seitsonen, S. Wendt, A. Morgante, E. Lundgren, M. Schmid, P. Varga, and G. Ertl, *Science* 287 (2000)



Also:

A. Böttcher, et al.,
Surf. Sci. 466, L811 (2000) ;
L. Zang and H. Kisch,
Angew. Chem. 112, 4075 (2000)

Ab initio atomistic thermodynamics

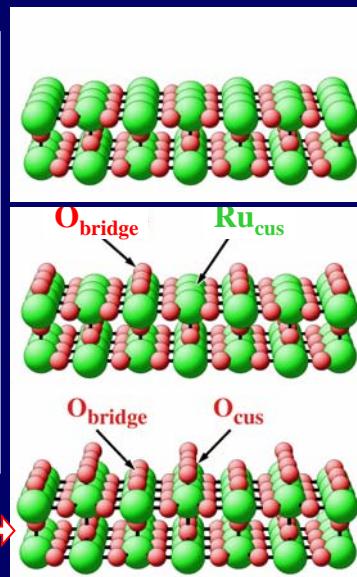
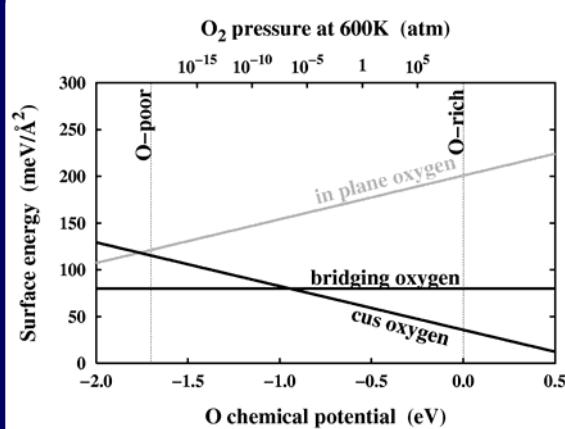


DFT (FP-LAPW; GGA)

$$\mu_{\text{O}}(T, p) = \frac{1}{2} \mu_{\text{O}_2}(T, p^0) + \frac{1}{2} kT \ln(p/p^0)$$

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

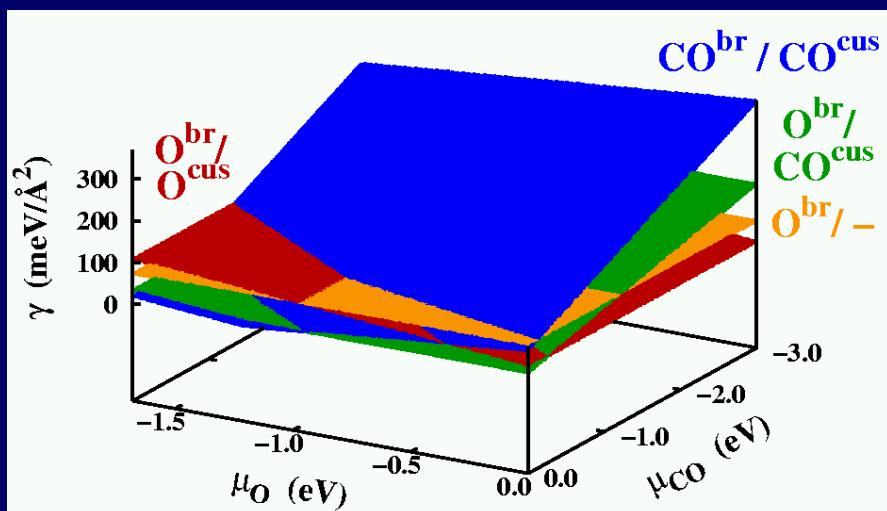
RuO₂(110) surface terminations



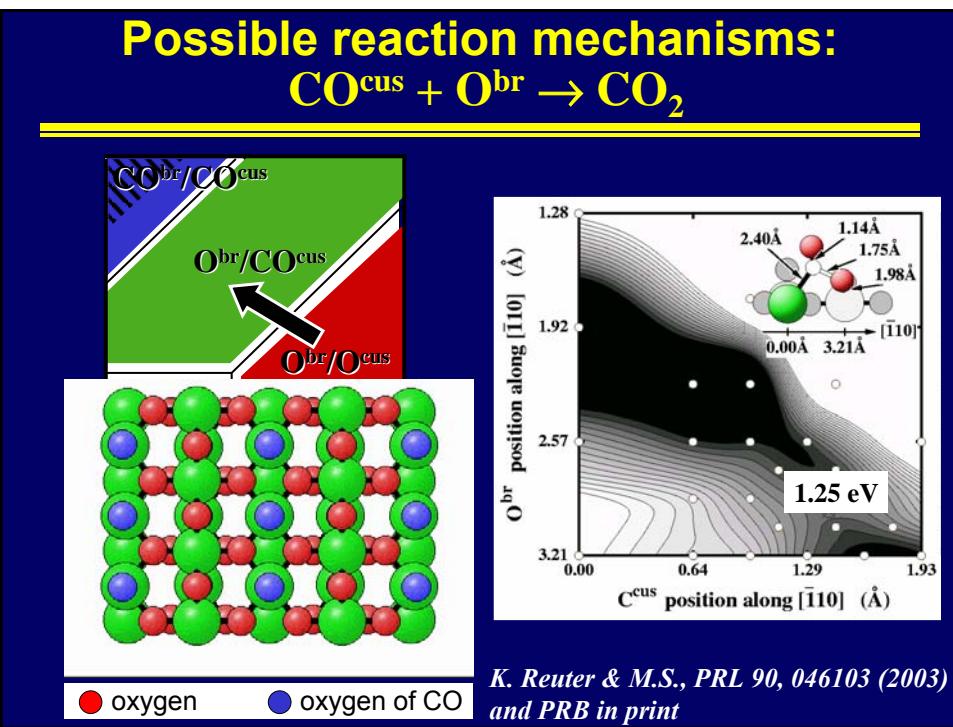
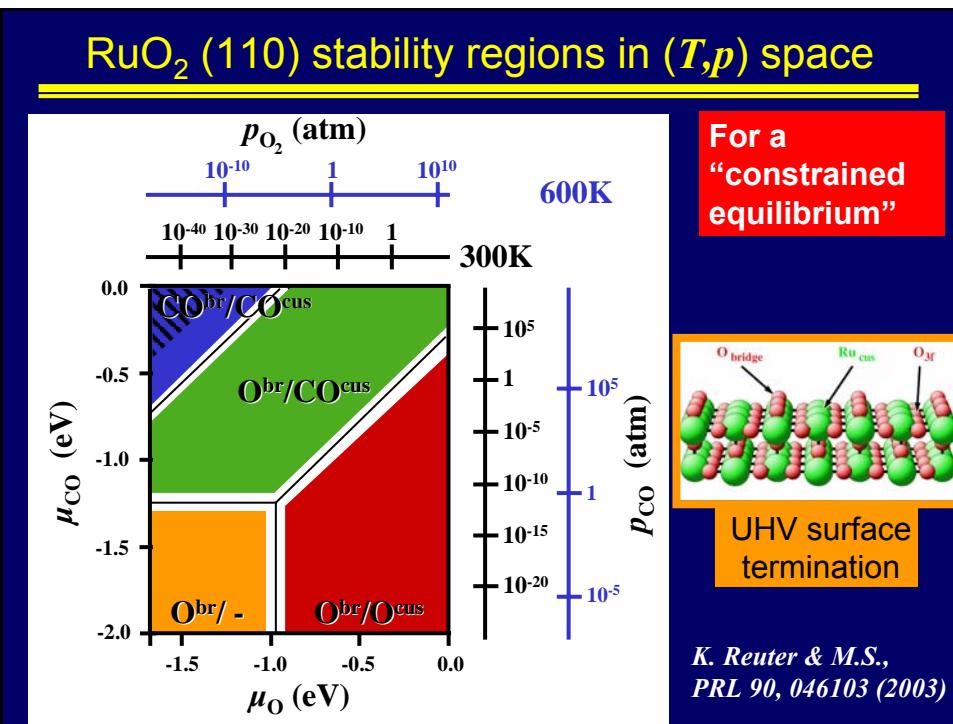
high pressure termination

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

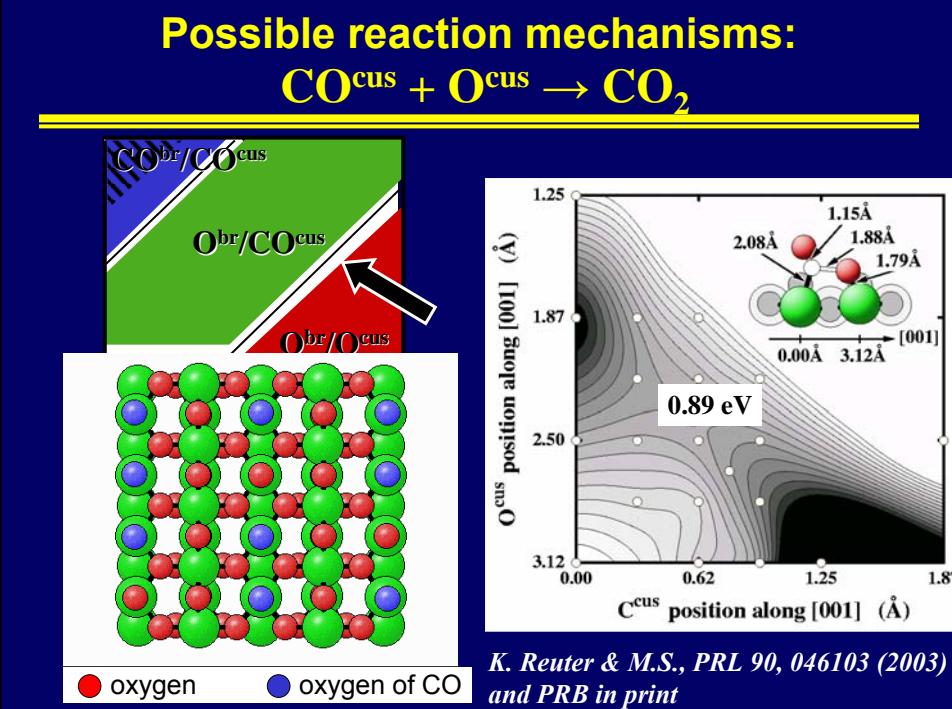
RuO₂ (110) surface structures with O₂ and CO in the gas phase



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



Possible reaction mechanisms:



Theory of the kinetics of catalysis

- 1) Analysis of all possibly relevant processes
- 2) Calculate the rates of all important processes

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

- 3) Statistical approach to describe
 - dissociation, adsorption, desorption
 - diffusion
 - reaction (CO_2 formation)
 - desorption of the product

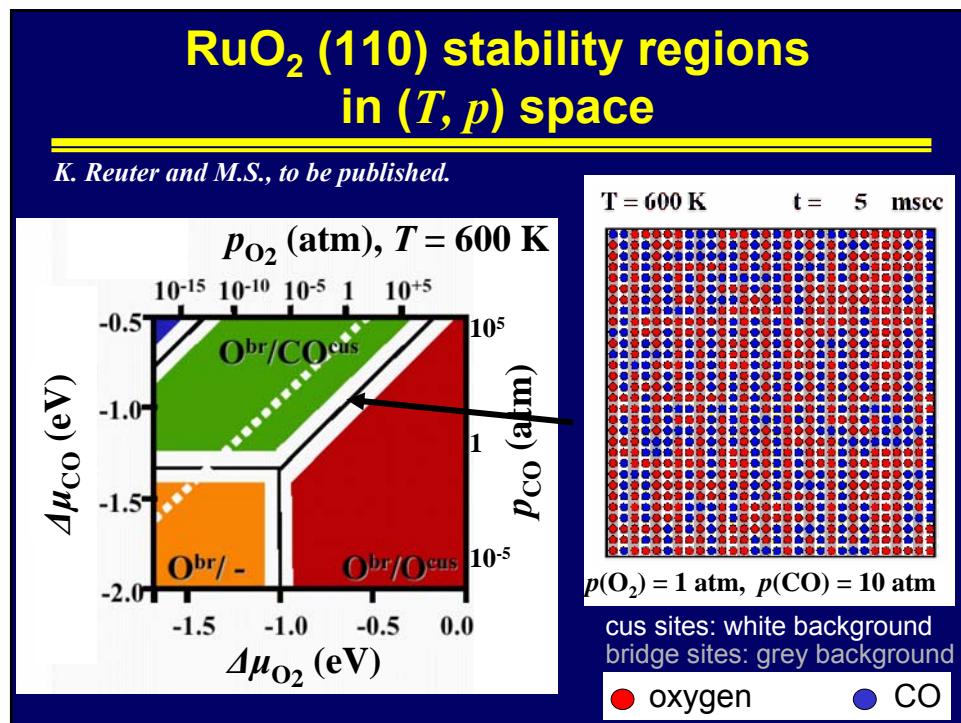
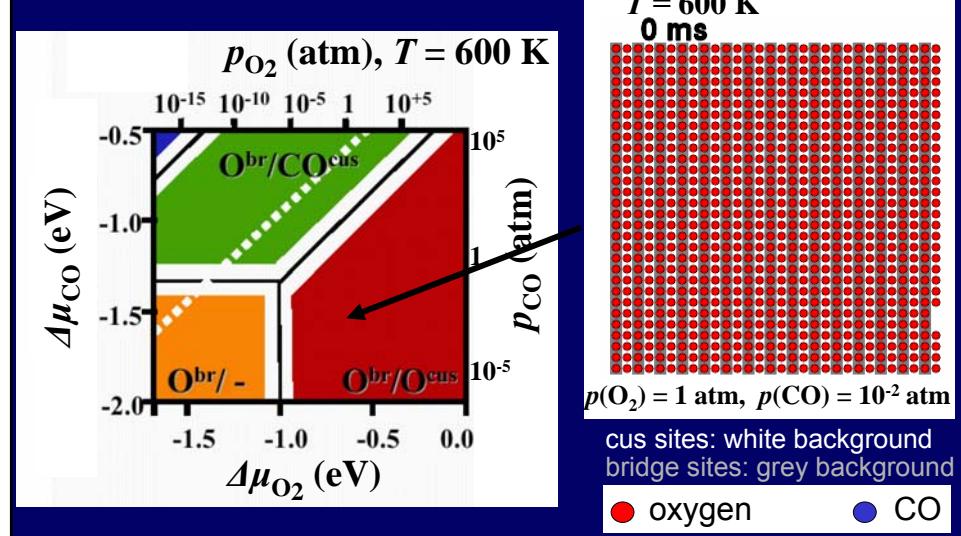
→ **kinetic Monte Carlo method**



movies

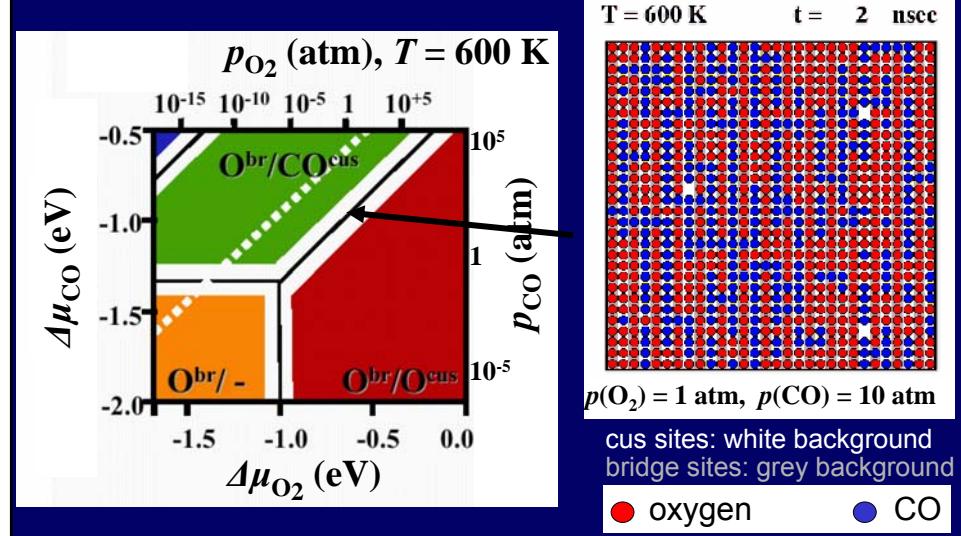
RuO₂ (110) stability regions in (T, p) space

K. Reuter and M.S., to be published.



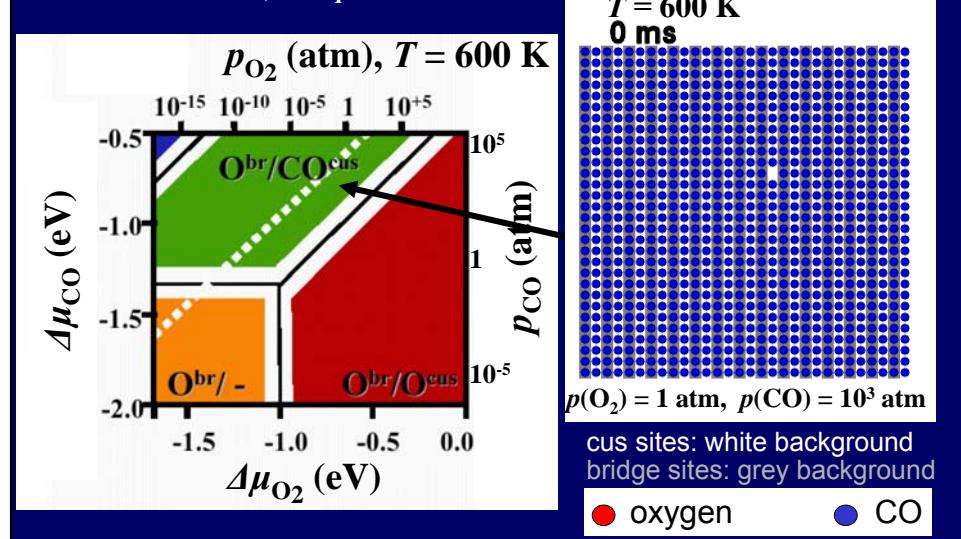
RuO₂ (110) stability regions in (T, p) space

K. Reuter and M.S., to be published.



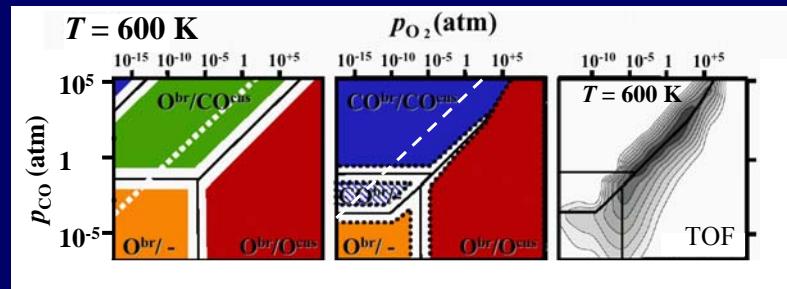
RuO₂ (110) stability regions in (T, p) space

K. Reuter and M.S., to be published.



RuO₂ (110) high reactivity regions

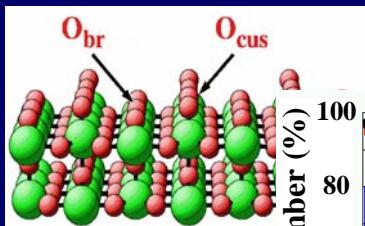
(bridging the pressure gap) *K. Reuter and M.S., to be published.*



- Most frequent: de- and adsorption of CO (mostly CO^{cus}).
- O desorbs “only” from cus sites (“only” as O₂).
- CO₂ formation: CO^{cus} + O^{cus} (0.9 eV), CO^{br} + O^{cus} (0.8 eV), CO^{cus} + O^{br} (1.2 eV). The rate is $r_{\text{CO}_2} = 10^{18} \text{ cm}^{-2} \text{ s}^{-1}$.

Site occupation statistics at the steady state

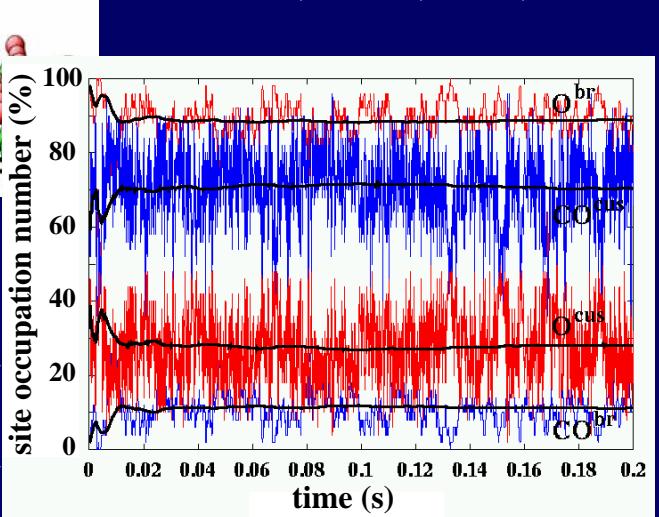
K. Reuter, D. Frenkel, and M.S., submitted.



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

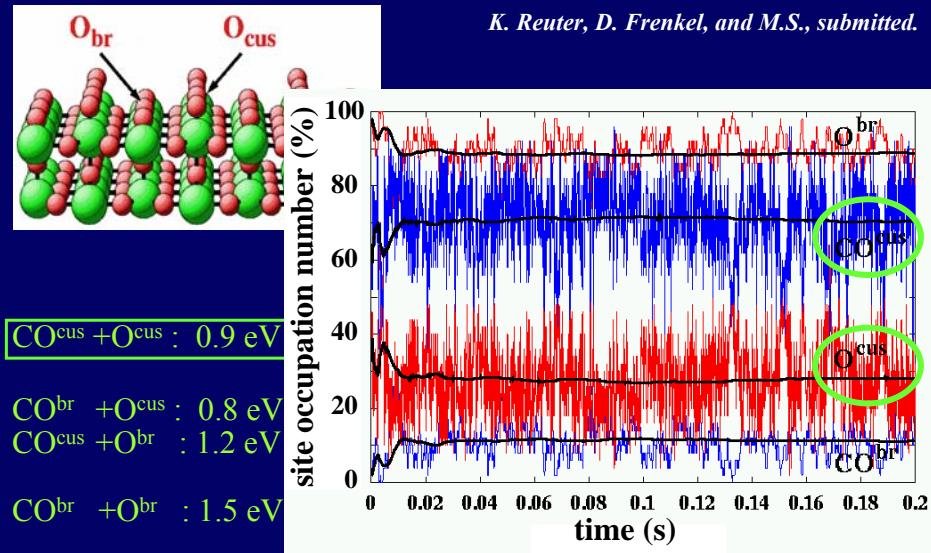
CO^{br} + O^{cus} : 0.8 eV
CO^{cus} + O^{br} : 1.2 eV

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



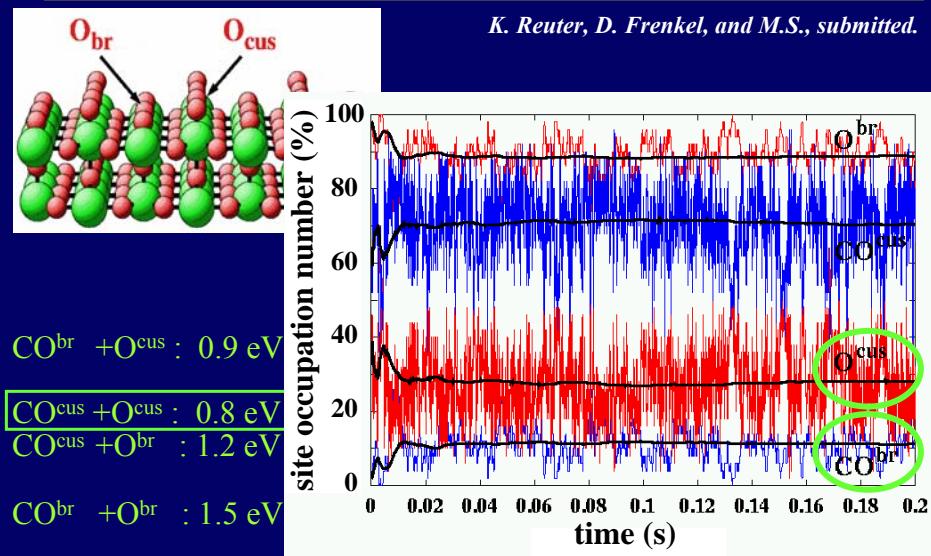
Site occupation statistics at the steady state

K. Reuter, D. Frenkel, and M.S., submitted.



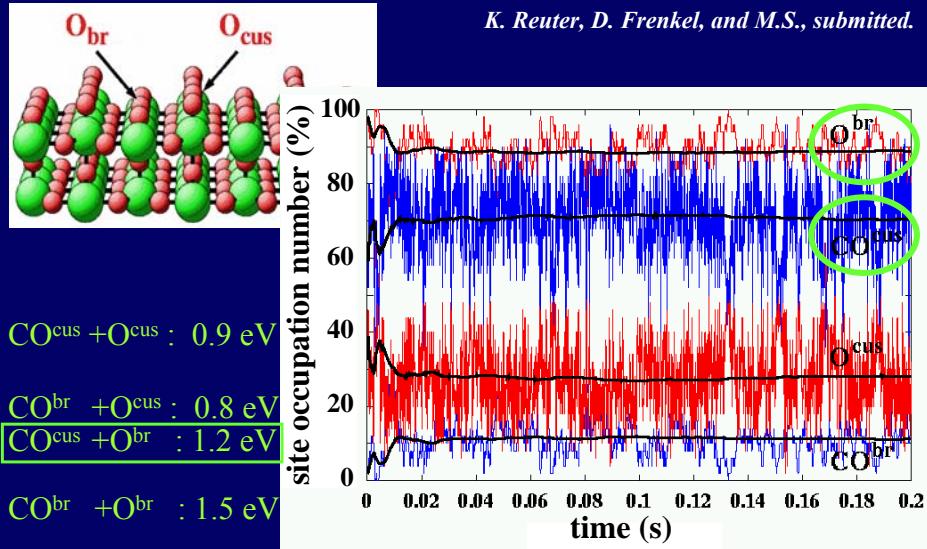
Site occupation statistics at the steady state

K. Reuter, D. Frenkel, and M.S., submitted.



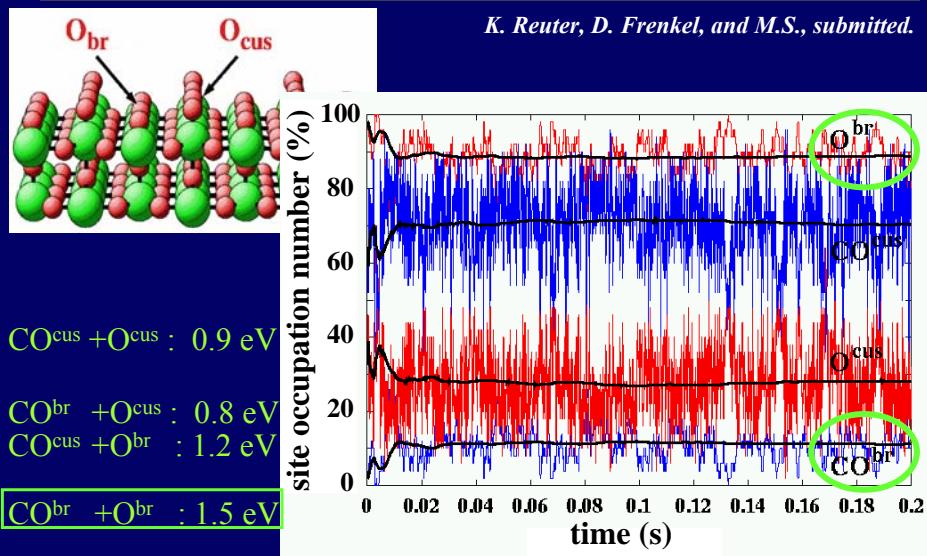
Site occupation statistics at the steady state

K. Reuter, D. Frenkel, and M.S., submitted.

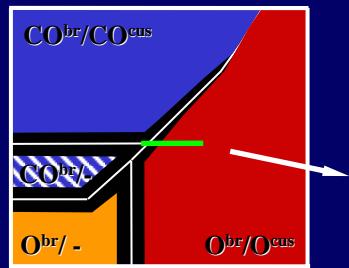


Site occupation statistics at the steady state

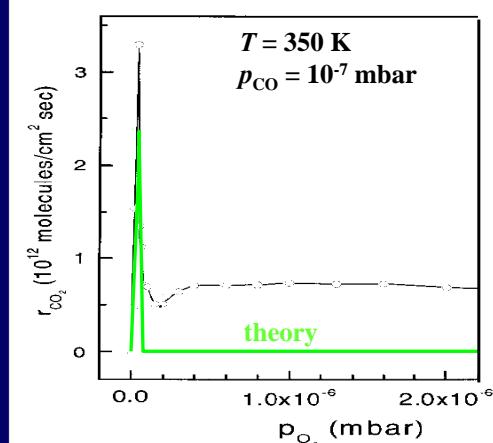
K. Reuter, D. Frenkel, and M.S., submitted.



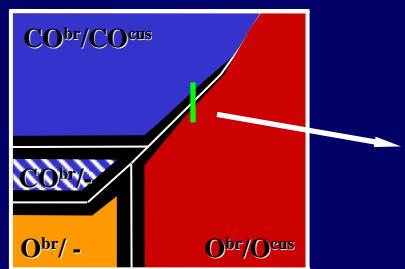
Comparison with experimental results



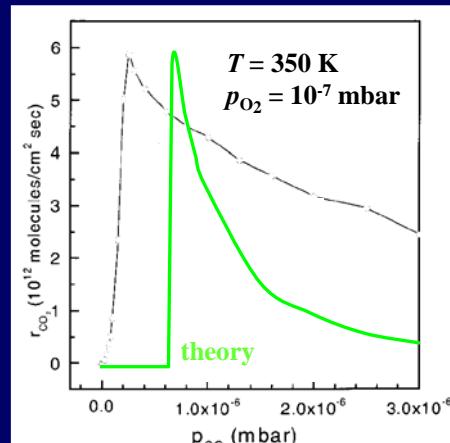
J. Wang, C.Y. Fan,
K. Jacobi, and G. Ertl,
J. Phys. Chem. B 106,
3422 (2002)



Comparison with experimental results

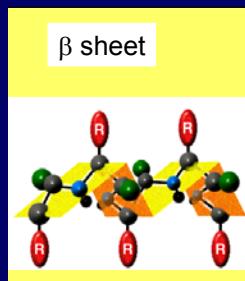
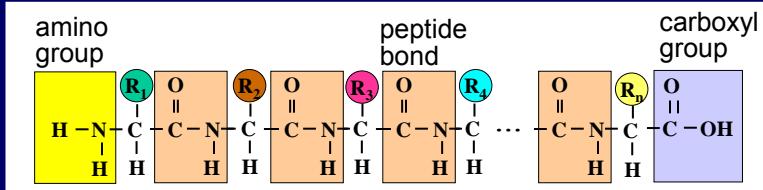
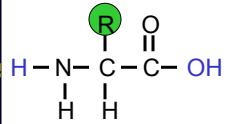


J. Wang, C.Y. Fan,
K. Jacobi, and G. Ertl,
J. Phys. Chem. B 106,
3422 (2002)

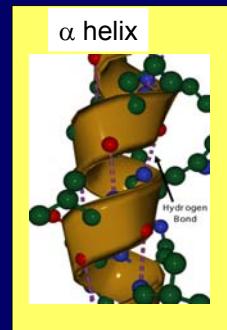


Stability of the α -helix

structure of proteins (peptide chains):

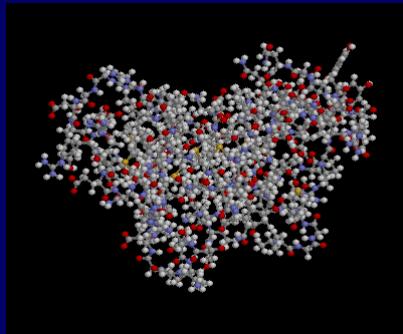


secondary
structure

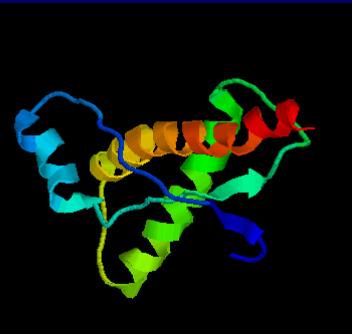


Folding of the peptide chain

peptide chain in the bovine prion protein



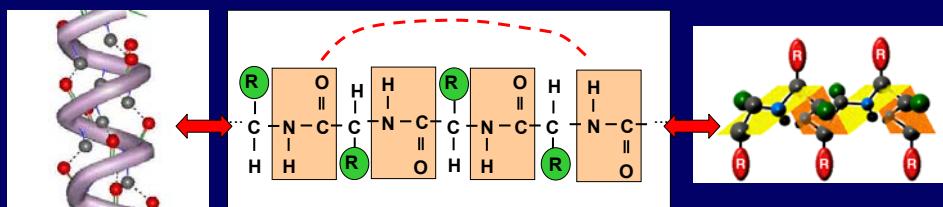
atomic structure



secondary and tertiary
structure

<http://www.rcsb.org/> -- pdb-id: 1QMO

Enthalpy of formation of a hydrogen Bond



$$\text{Enthalpy of formation: } \Delta H^N = E_{\sigma}^N - E_{\sigma}^{N-1} - \mu_{\text{peptide}}$$

poly alanine (R = methyl group = CH_3)

sheet (extended structure) as "reservoir"

α -helix:

"back bone" costs : $\Delta H_{\text{bb}}^N \approx 6.5 \text{ kcal/mol}$ for all N

H-bond gain : $\Delta H_{\text{H-bond}}^N = -2.7 \text{ kcal/mol}$ for $N=4$
 $= -9.5 \text{ kcal/mol}$ for $N=\infty$

→ **hydrogen bond is strongly cooperative**

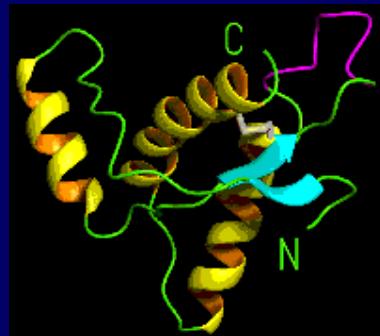
J. Ireta et al., J. Phys. Chem. B, in print.

peptide chain in the bovine prion protein



http://cyber-dyne.com/~tom/reverse_chron.html

peptide chain in the bovine prion protein



http://cyber-dyne.com/~tom/reverse_chron.html

Electronic Structure Theory
(Density Functional Theory \longrightarrow QMC)

→ **Potential Energy Surface**

Dynamics of the Nuclei
along this **PES**

Statistical Mechanics

Thermal
Equilibrium
Structures

Real World

The people behind the work



Cathy Stampfl



Joel Ireta



Karsten Reuter



et al. ...



Peter Kratzer

<http://www.fhi-berlin.mpg.de/th/th.html>