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

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

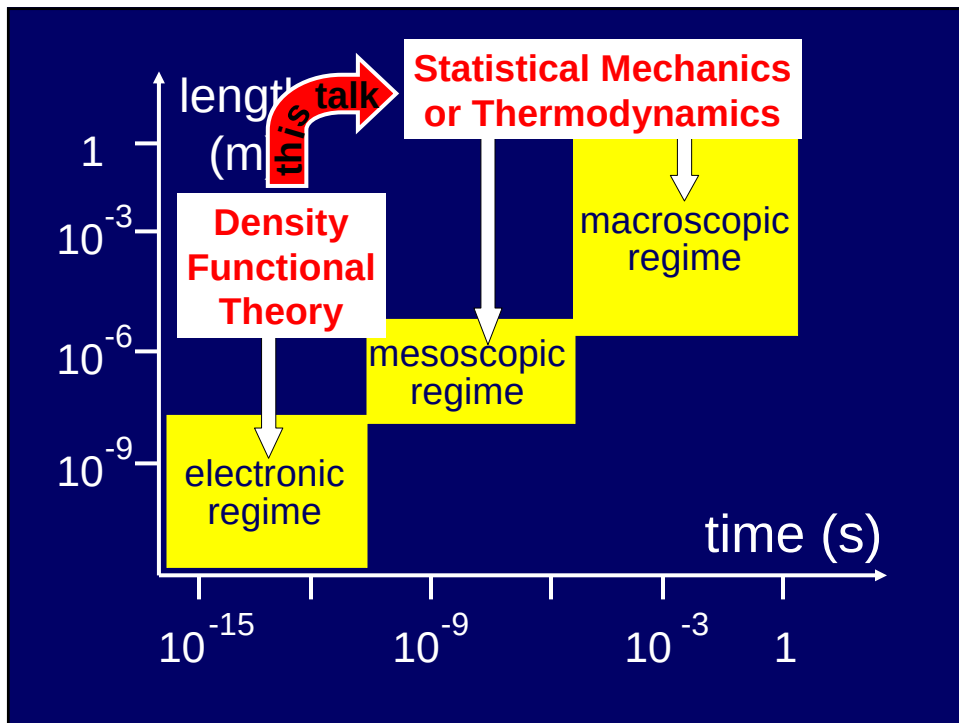
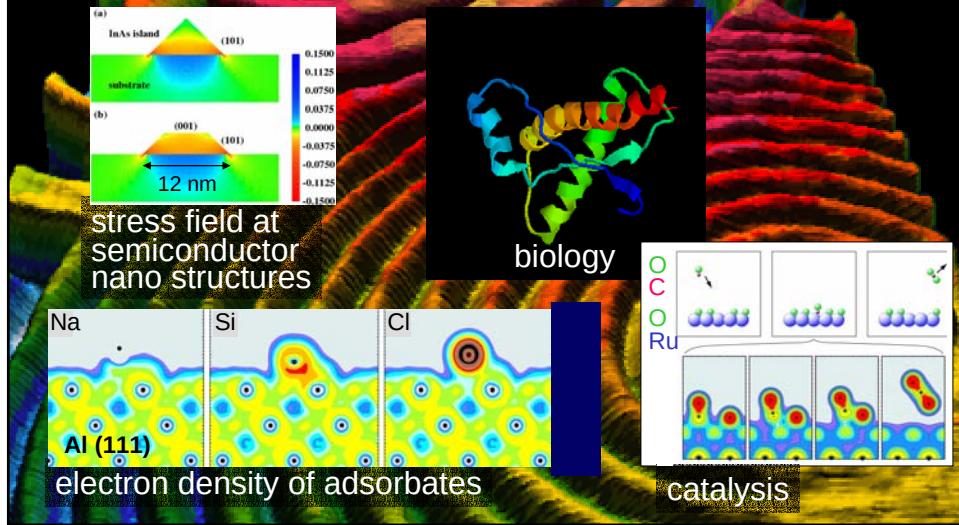
Parts I - II - III

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Berlin, Germany

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):

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

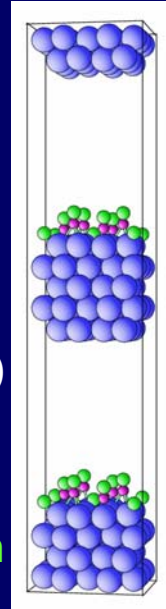
with **local-density approximation**
or **generalized gradient approximation**

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].

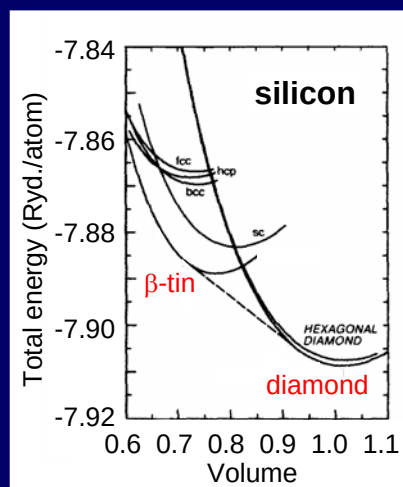


Methods

- 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)

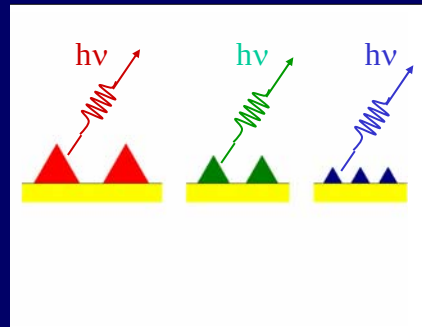
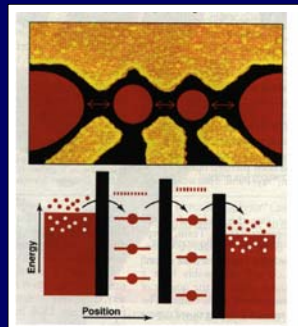
see also:
V.L. Moruzzi, J.F. Janak,
and A. R. Williams
*Calculated Electronic
Properties of Metals*
Pergamon Press (1978)

Self-Assembly of Nano-Scale Structures at Semiconductor Surfaces

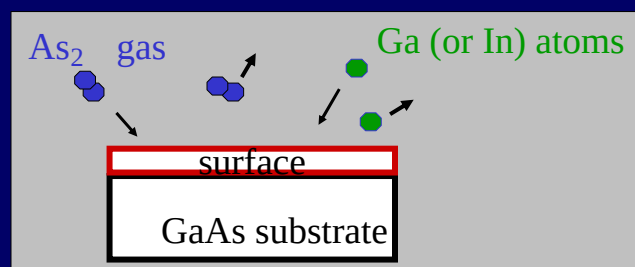
Motivation:

Single-electron transistor

LEDs and
laser diodes



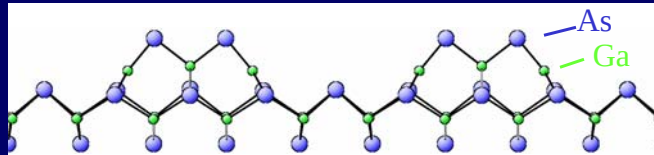
Microscopic processes controlling the growth -- Example: III-V semiconductors



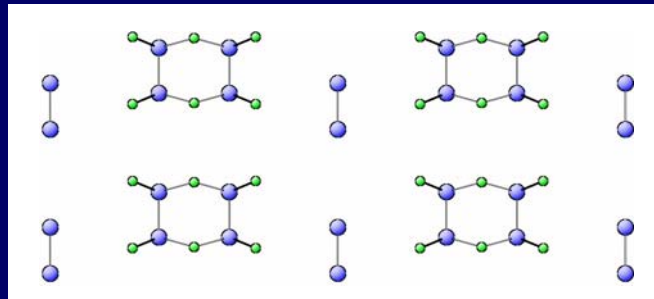
- | | |
|----------------------------|------------------------------------|
| 1) deposition of Ga and As | 5) adsorption of As_2 ? |
| 2) adsorption of Ga | 6) dissociation of As_2 ? |
| 3) diffusion of Ga | 7) diffusion of As |
| 4) desorption of Ga | 8) desorption of As |
| | 9) island nucleation |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

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

side
view



top
view

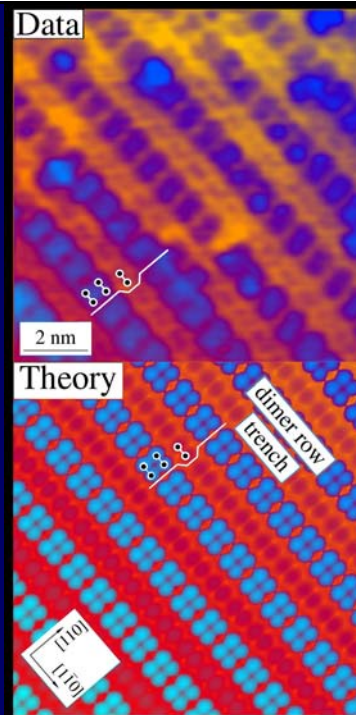


STM Imaging of GaAs(001)

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

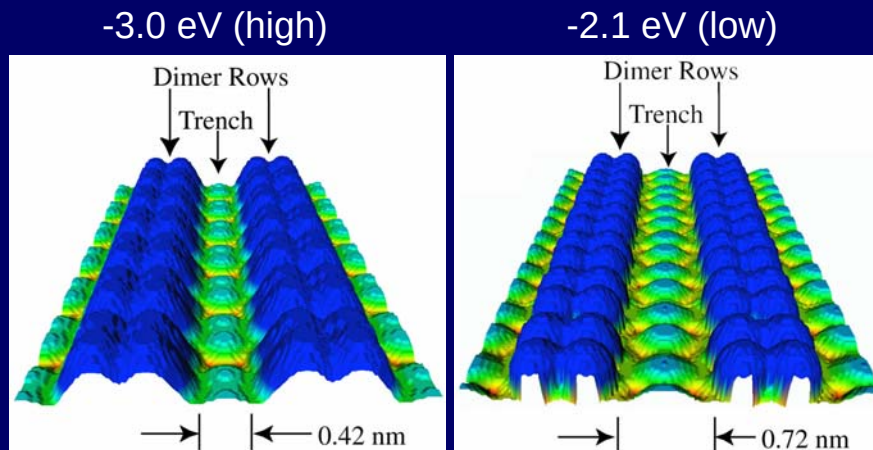
simulated image:
local density of states
integrated to 0.3 eV
below the valence
band maximum →

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



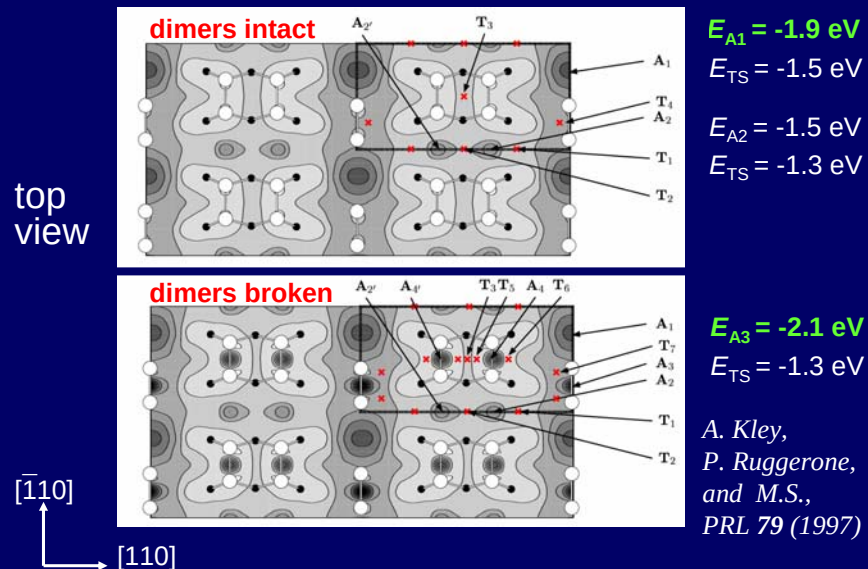
Voltage Dependence of the STM Current

STM Simulation

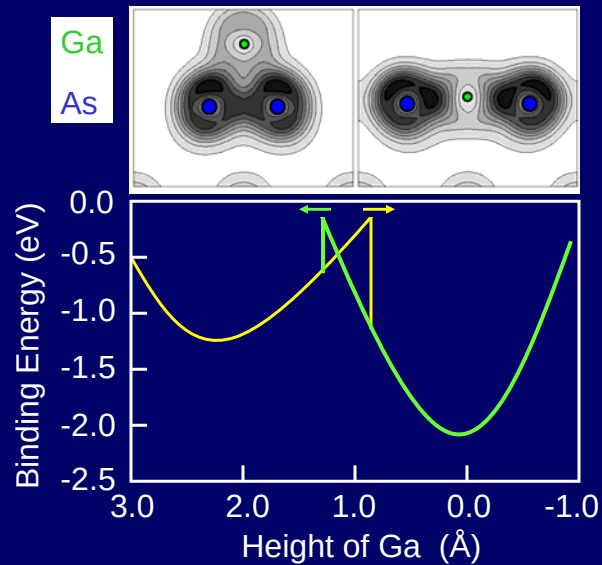


LaBella, Yang, Bullock,
Thibado, Kratzer & Scheffler,
PRL 83, 2989 (1999).

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



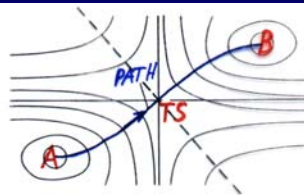
Unusually stable site for Ga adatom inside the trench-site As-dimer



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

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

Transition State Theory



Transition state theory

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

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

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

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

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

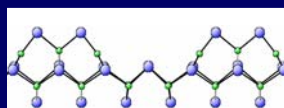
- deposition
- diffusion
- nucleation
- growth



kinetic Monte Carlo method

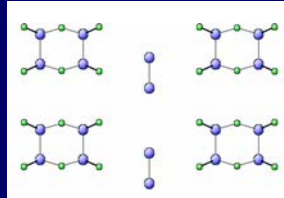
Adsorption, diffusion, island nucleation, and growth of GaAs

side
view

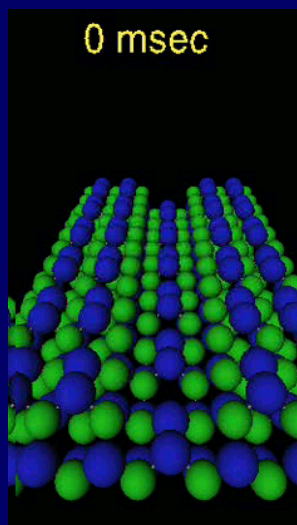


Ga
As

top
view



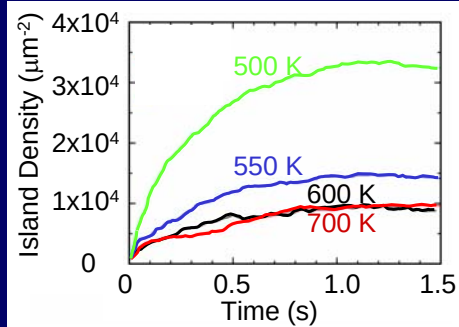
1/60 of the full simulation cell
As₂ pressure $\approx 1.33 \times 10^{-8}$ bar
Ga deposition rate = 0.1 ML/s
T = 700 K



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

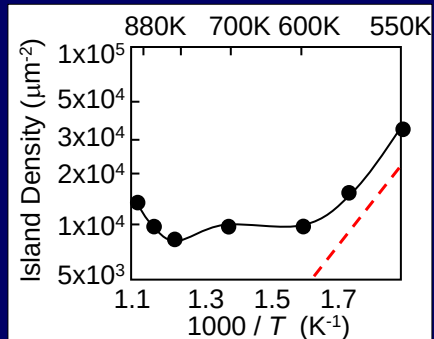
Island density

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

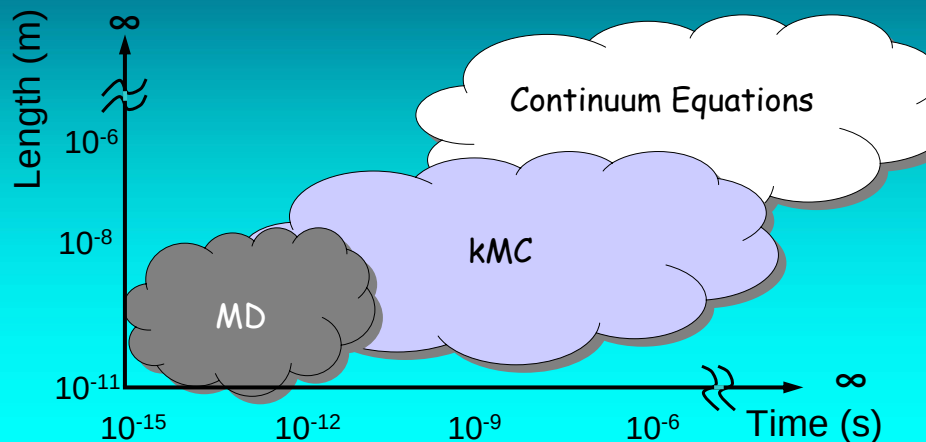


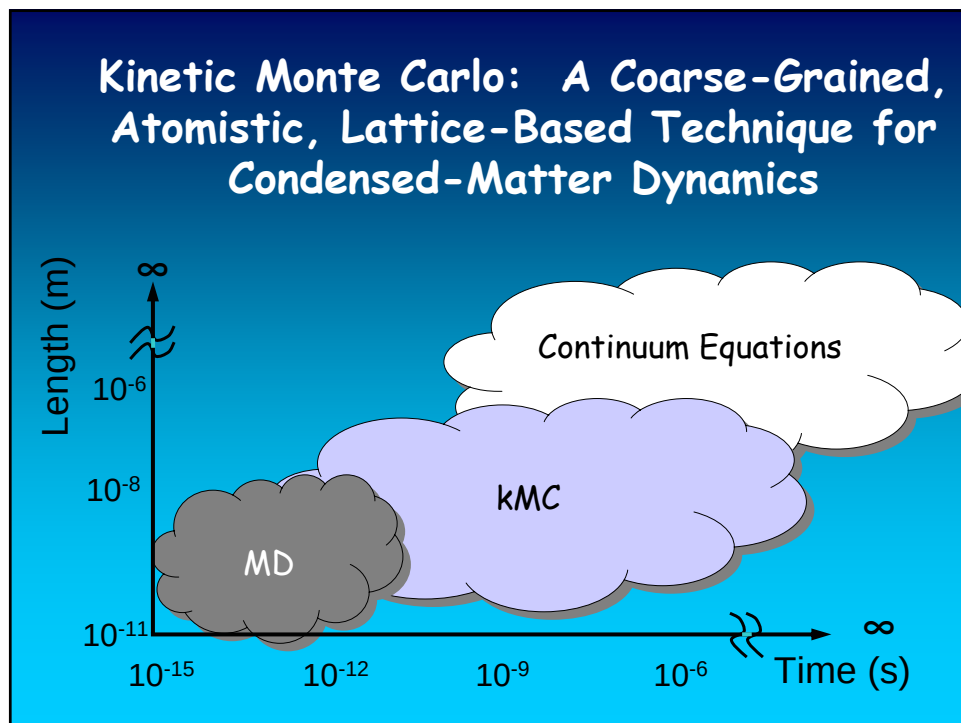
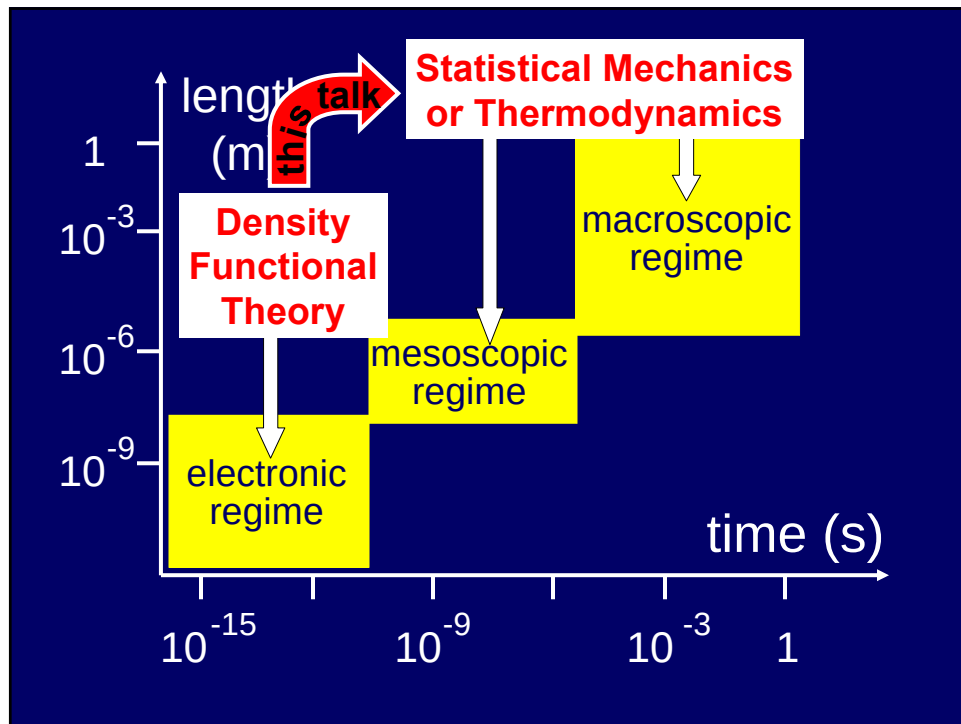
$\log_{10}$ of island density does not increase linearly with $1/T$: Unusual increase of island density with increasing T (for $T > 800$ K).

As_2 pressure
= 1.33×10^{-8} bar
Ga deposition rate
= 0.1 ML/s

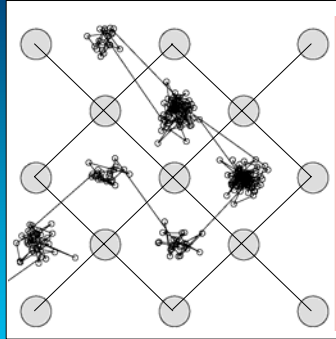


Kinetic Monte Carlo: A Coarse-Grained, Atomistic, Lattice-Based Technique for Condensed-Matter Dynamics

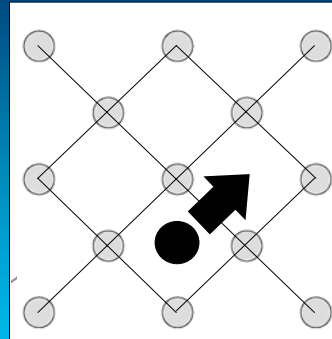




Kinetic Monte Carlo: Coarse-Graining MD



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



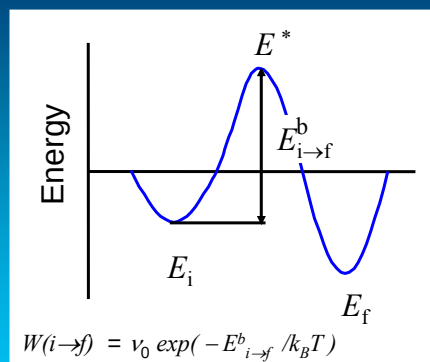
kMC: Coarse-Grained
Hops

KMC Transition Probabilities and the Detailed-Balance Criterion

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

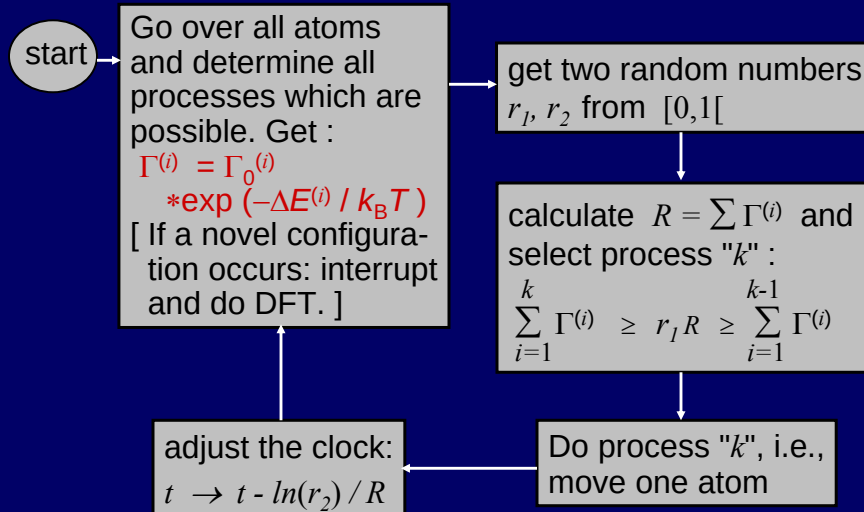
Metropolis MC Satisfies Detailed
Balance, but not Kinetics

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



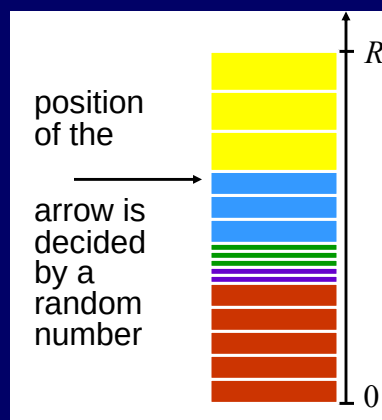
TST Satisfies Detailed
Balance and Kinetics

Flowchart of kinetic Monte Carlo Simulation



→ unsuccessful processes are avoided

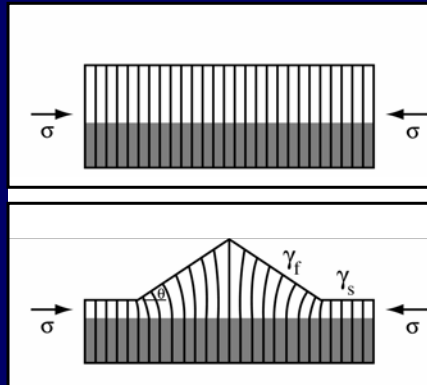
Sketch of the kMC Approach



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.

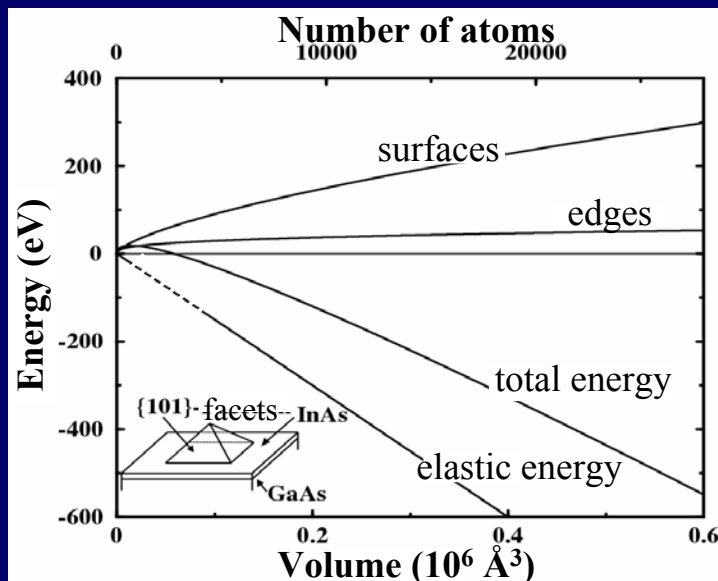
Stranski-Krastanow morphology as one way to reduce misfit strain energy



e.g.
InAs on
GaAs

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

Equilibrium Shape of Quantum Dots

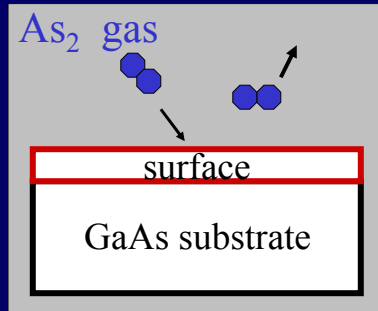


*L. Wang,
P. Kratzer,
and M.S.,
PRL 82
(1999)*

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:**

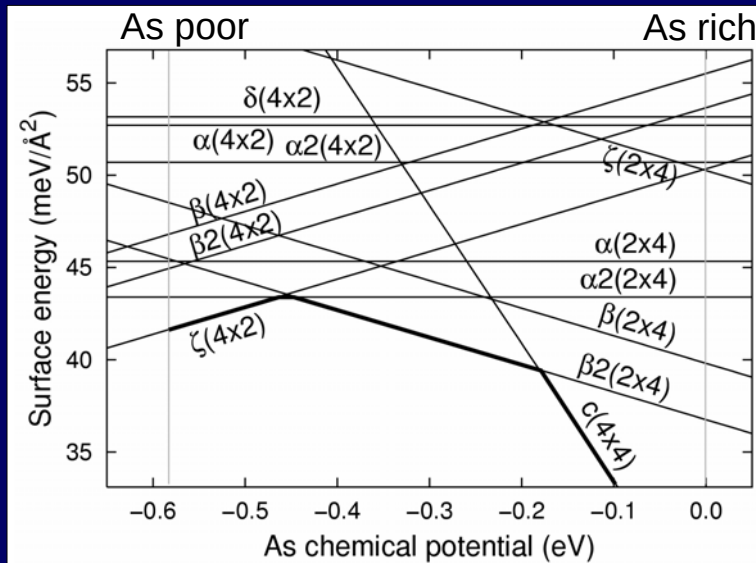
$$\mu_{\text{As}}(T, p) = \frac{1}{2} \mu_{\text{As}_2}(T, p^0) + \frac{1}{2} kT \ln(p/p^0)$$

ab initio atomistic thermodynamics

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

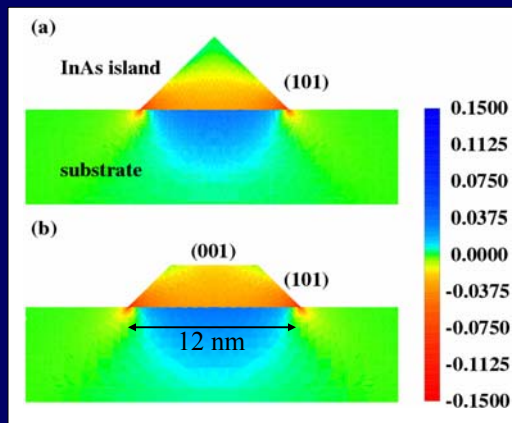
Reuter and M. S., Phys. Rev. B 65, 035406 (2002); PRL 90, 046103 (2003).

Surface Energies of Clean GaAs (001)

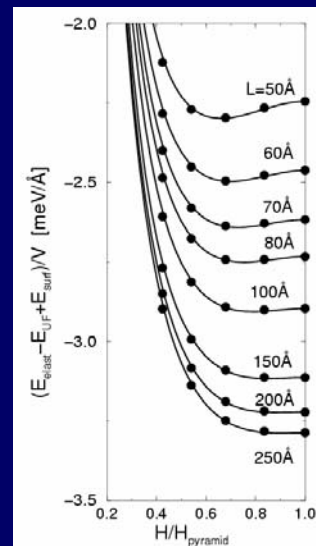


Sung-Hoon Lee, W. Moritz, & M.S., PRL 85, 3890 (2000)

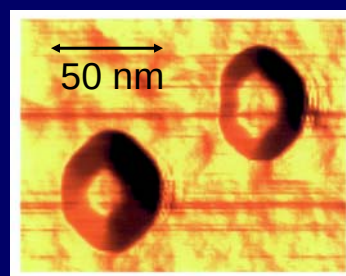
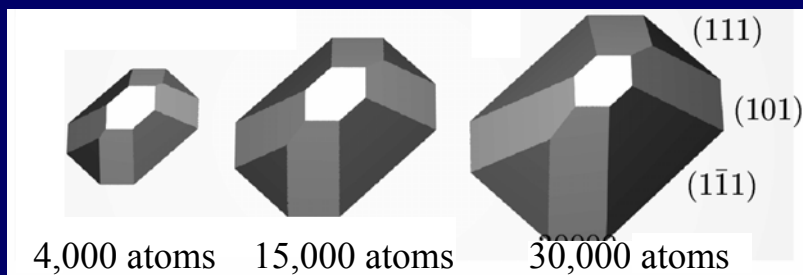
Stress Tensor at strained InAs Islands on GaAs



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



InP Quantum Dots on GaP(001)

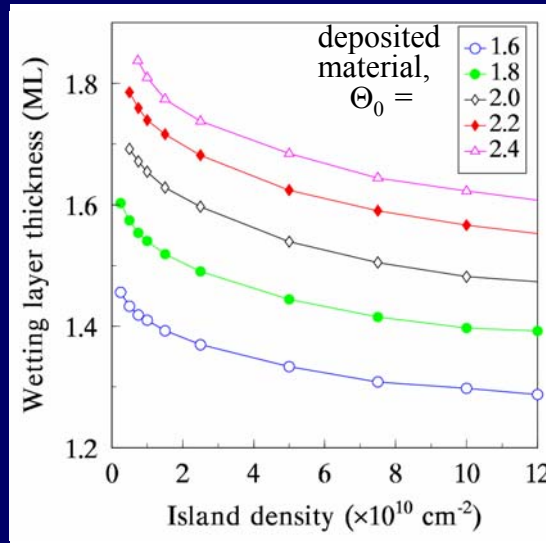


*Q. Liu, E. Pehlke,
N. Moll, and M.S.,
PRB 60 (1999)*

InP islands on GaInP
grown by MOVPE

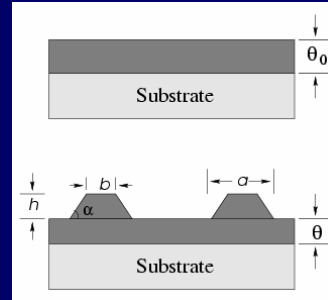
Samuelson et al. (1996)

Thickness of the Wetting Layer Depends on the Island Density



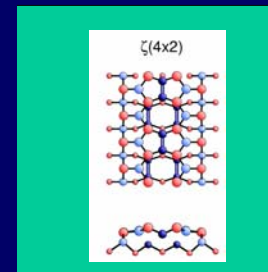
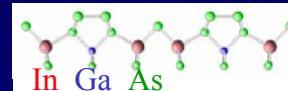
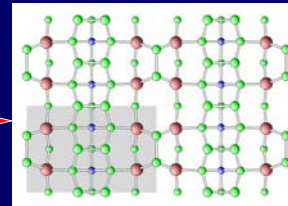
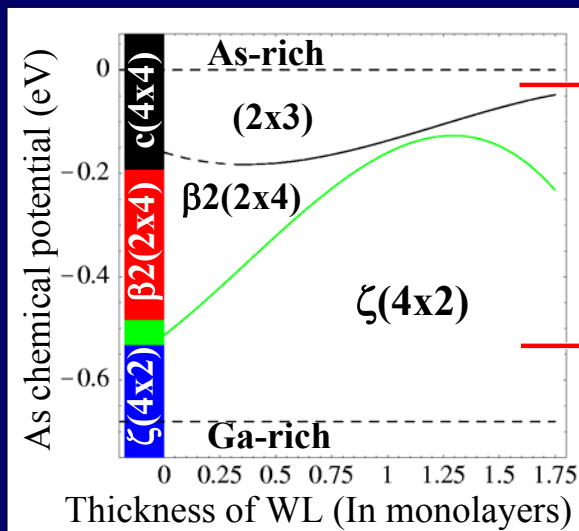
InAs on GaAs

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



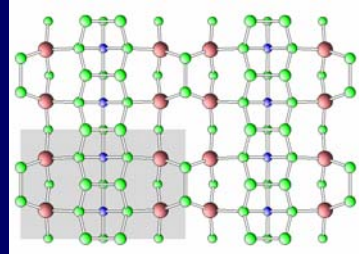
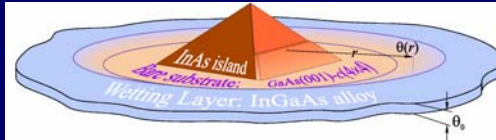
L. Wang, P. Kratzer, & M.S., PRL 82 (1999)

Reconstruction of the Wetting Layer



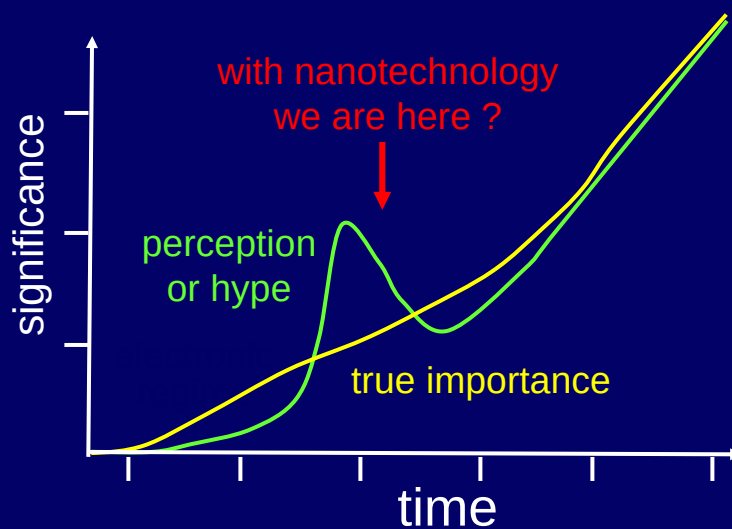
Small islands grow fast, and big (coherent) quantum dots develop a "repulsive ring"

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

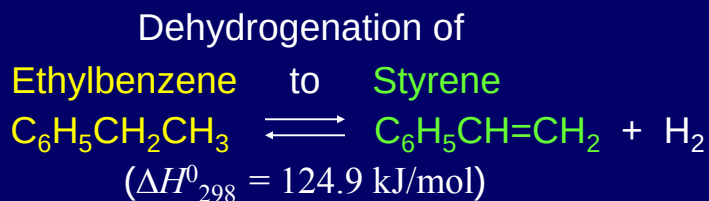


E. Penev, P. Kratzer, & M.S.,
submitted (2002)

Emerging new technologies



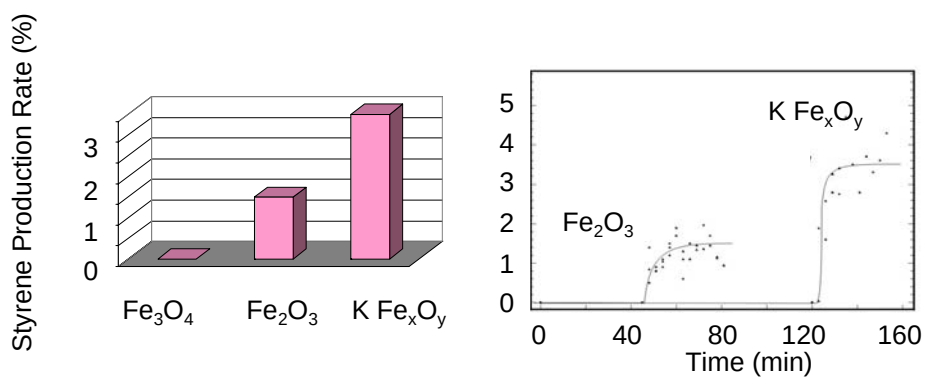
Commercial Process of Styrene Production



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%

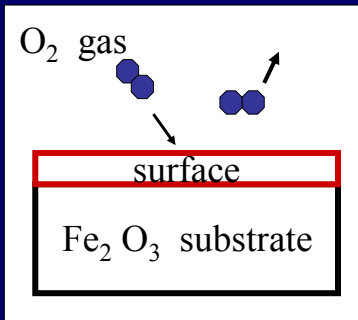
Catalytic Activity



Stoichiometry and Structure of the Surface depend on the Environment

(atomic chemical potentials)

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



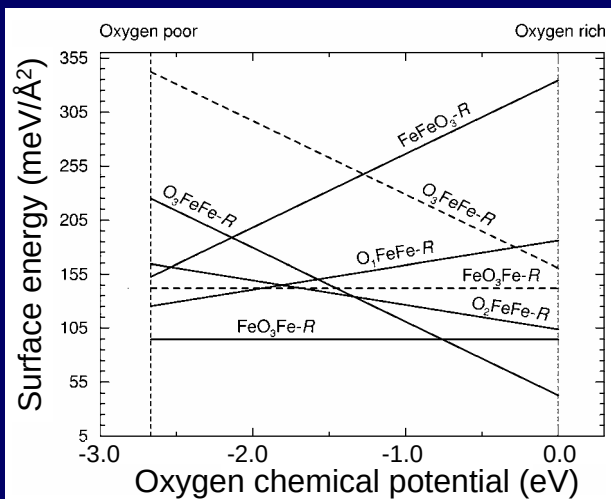
$$2 \mu_{\text{Fe}} + 3 \mu_{\text{O}} = E^{\text{bulk}}(\text{Fe}_2\text{O}_3)$$

Only one independent
variable:

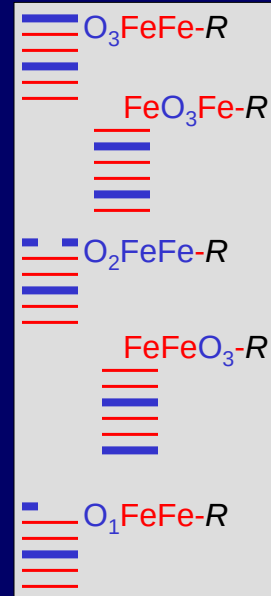
$$\begin{aligned} \mu_{\text{O}}(T, p) = \\ = \frac{1}{2} \mu_{\text{O}_2}(T, p^0) + \frac{1}{2} kT \ln(p/p^0) \end{aligned}$$

ab initio atomistic thermodynamics

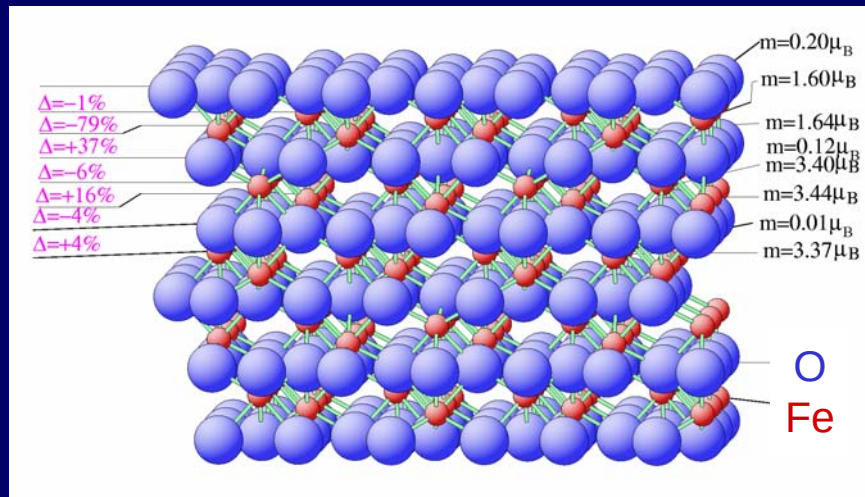
Fe₂O₃ (0001) Surface Terminations



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

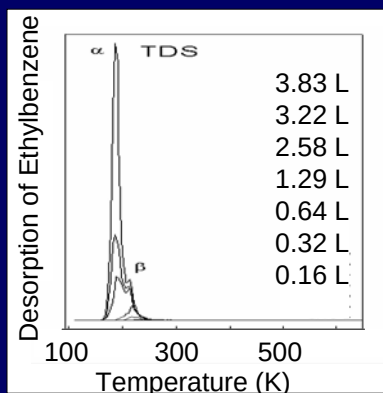


Fe₂O₃ (0001) O-terminated Surface



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

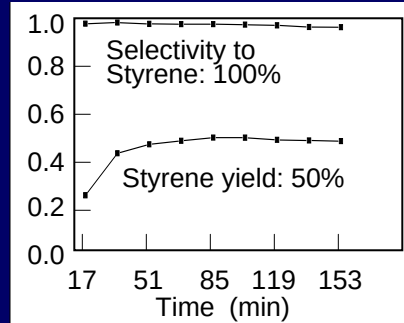
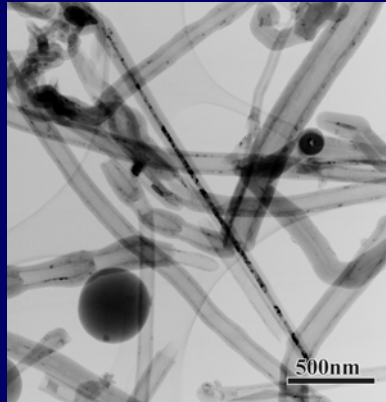
What is the active catalyst ?



C. Kuhrs and R. Schlögl,
to be published

- 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 ?

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?

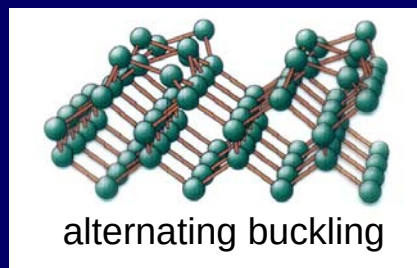
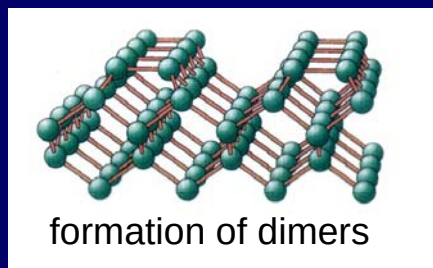
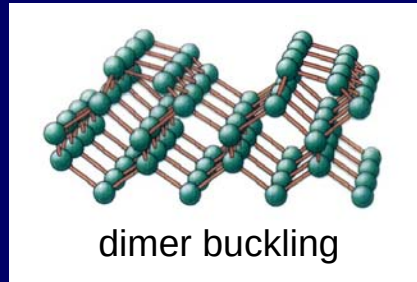
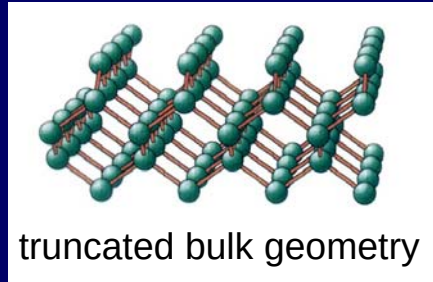
- Properties that are given by ensemble averages or ruled by the statistical interplay of many processes are well described by DFT-GGA.
- Errors in total energies can be noticeable. Even for energy *differences* they can be as large as several tenths of an eV. And sometimes this is indeed crucial.

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)

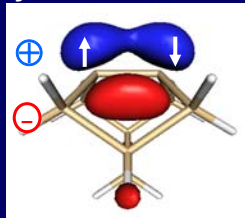
Dimerization and dimer buckling at Si(001)



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

"A negative U system" ?

HOMO of symmetric dimer

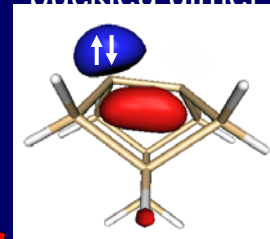


favored by MCSCF (clusters)

Which configuration is the ground state ?

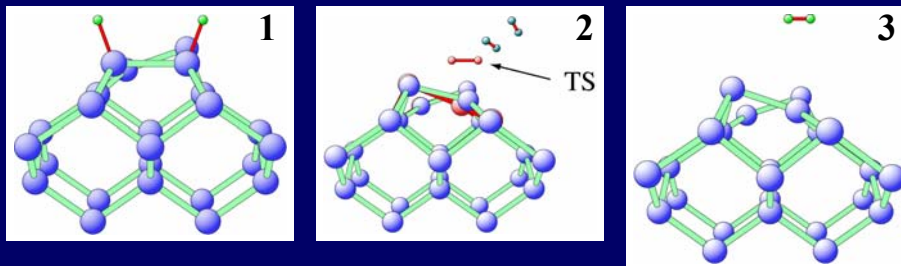
this one

HOMO of buckled dimer



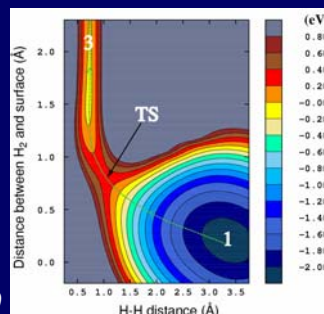
favored by DFT (slabs)

The H₂ / Si(001) energy barrier puzzle

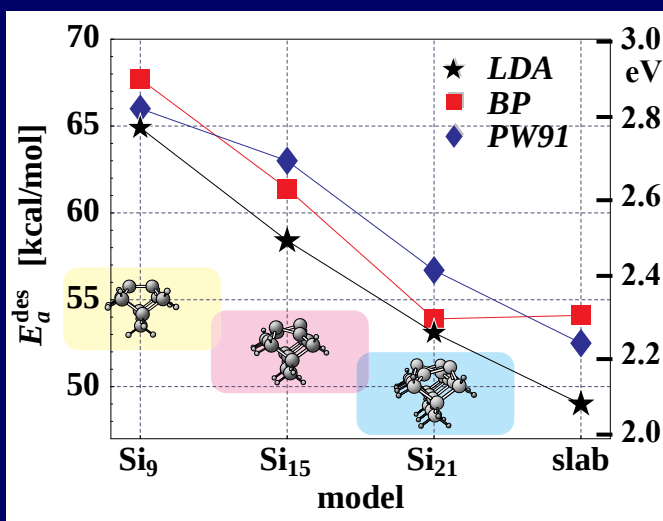


- CI-cluster and DFT-slab calculations give very different descriptions.
- Neither of them agrees with experiment.

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

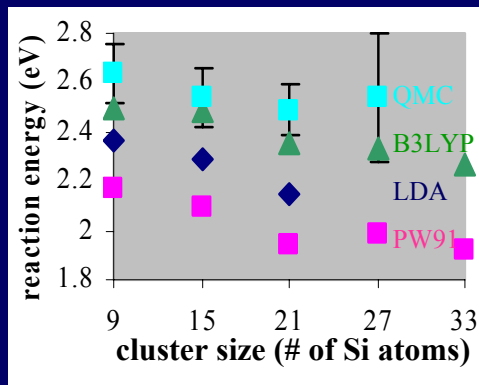
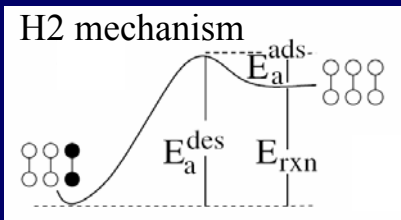
MCSCF

Variational QMC
iterative improvement of
Jastrow factor

Diffusion QMC
(starting from VMC
trial wave function)

Correction of the xc Energy

H₂ mechanism

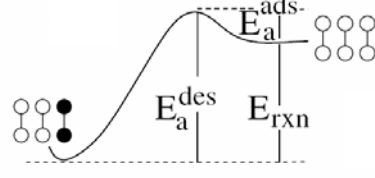


$$\Delta E = E_{\text{cluster}}(\text{QMC}) - E_{\text{cluster}}(\text{GGA}) = 0.48 \pm 0.1 \text{ eV}$$

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

Checking the quality of the xc treatment

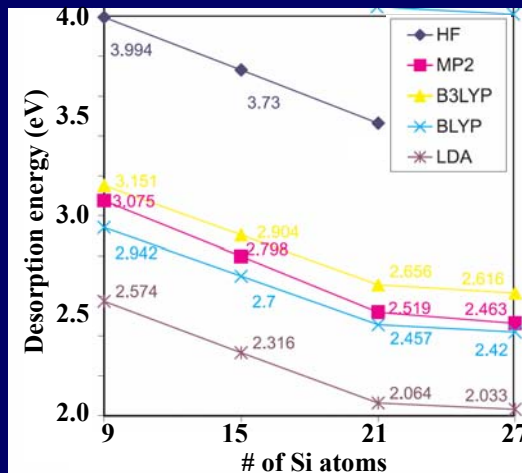
H2 mechanism



- 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 !

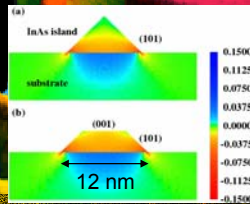
Sometimes corrections are necessary. The xc energy, E_{xc} , is a functional of the density, but maybe **impossible to handle as such**. Maybe, for the accuracy we need, we have to use a "detour" (we already do so for $T_s[n]$).

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} :
$$\Delta E^{xc} = E_{\text{cluster}}^{\text{WF}} - E_{\text{cluster}}^{\text{DFT-LDA}}$$

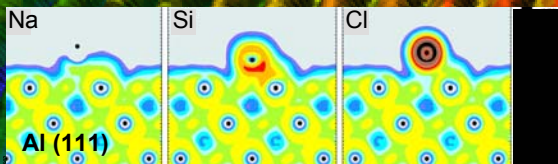
Nanometer-scale physics -- the examples of semiconductor quantum dots and heterogeneous catalysis



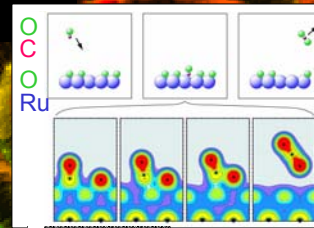
stress field at semiconductor nano structures



biology

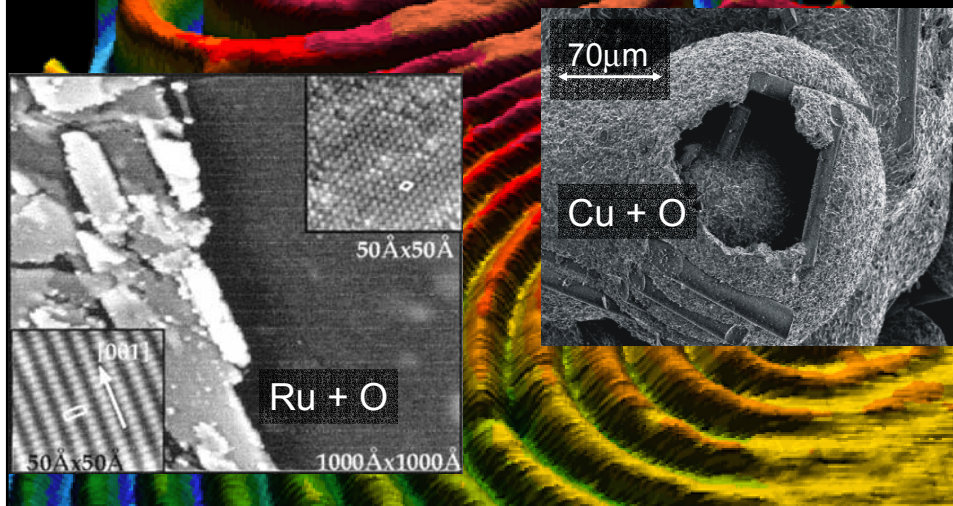


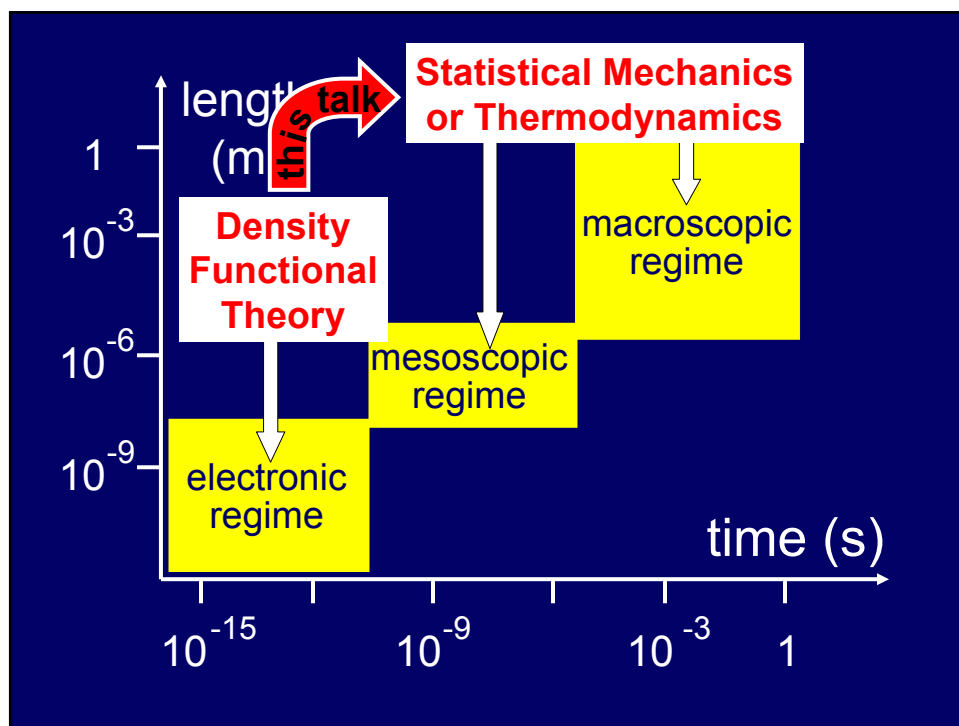
electron density of adsorbates



catalysis

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

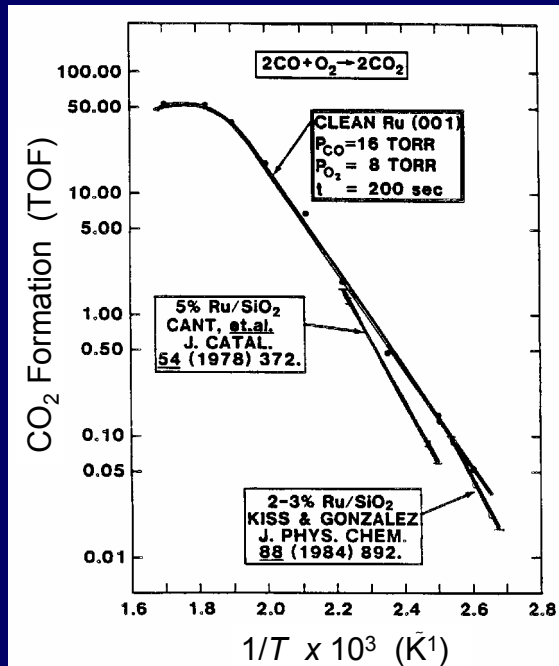




Oxidation catalysis, e.g.:



A "simple", prototypical surface chemical reaction

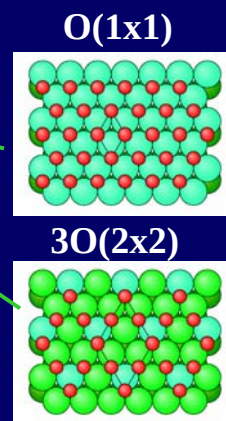
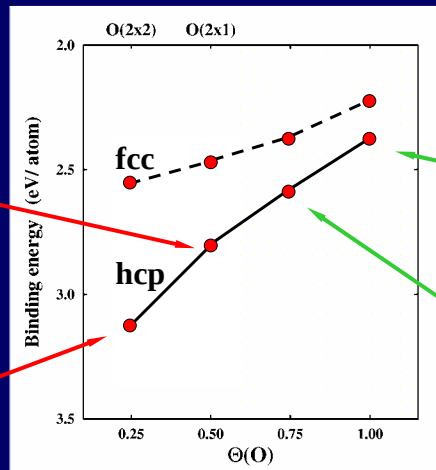
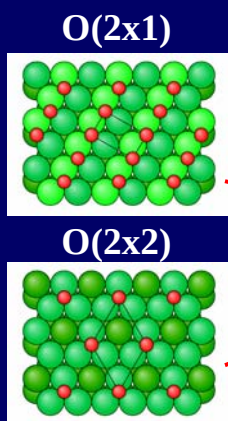


CO₂ formation
at Ru supported
catalysts and
Ru single crystals.

At UHV condi-
tions Ru is **least**
active for CO
oxidation. At
high-pressure
conditions it is
best.

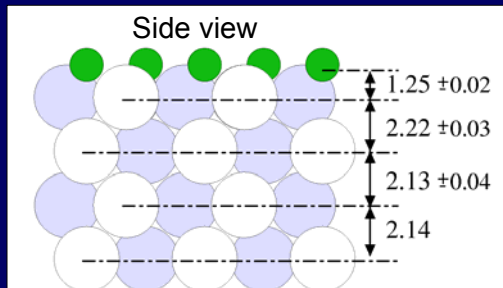
Oxygen Adsorption on Ru(0001)

UHV $\dashrightarrow$ High pressure



C. Stampfl and M. Scheffler, PRB 54, 2868 (1996)

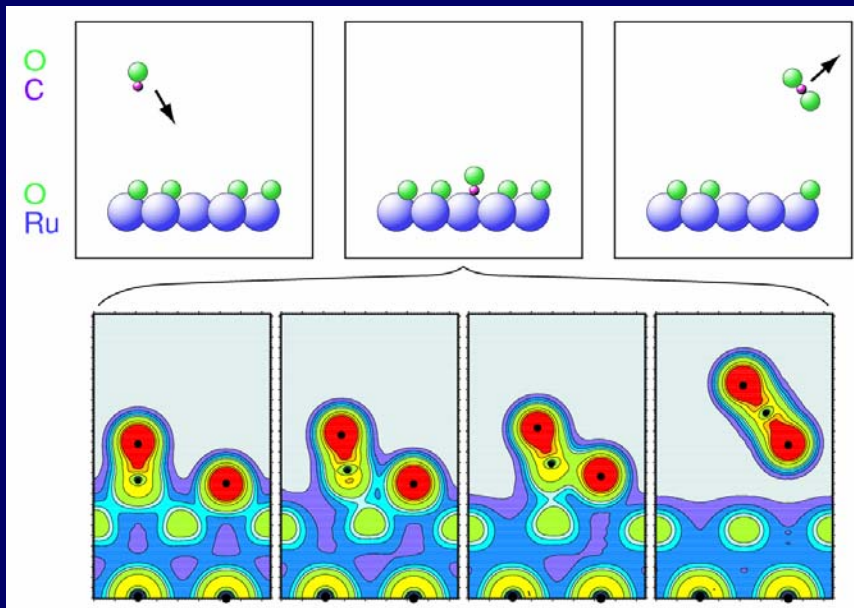
Prediction of new (unexpected) structures. Example: (1x1)-O/Ru(0001)



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 ₁ -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)*

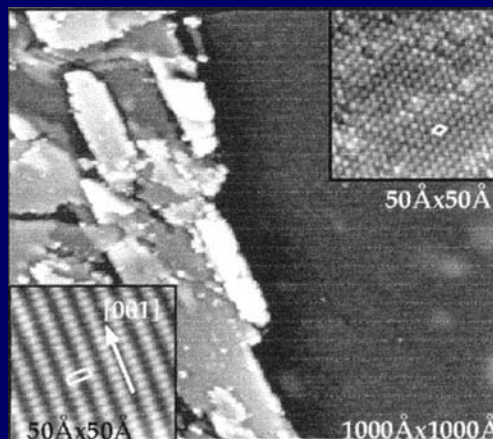
Transition -metals/ oxides as oxidation catalysts ? !

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

Also:

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

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



Ab initio atomistic thermodynamics



“constrained
equilibrium”



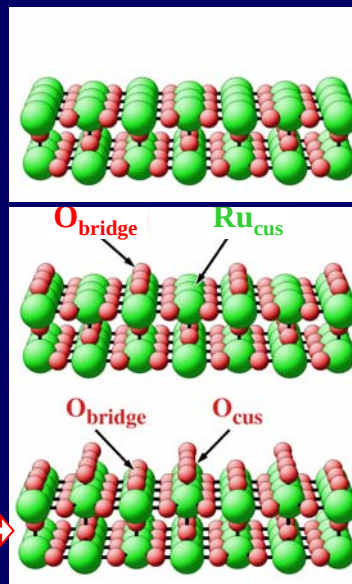
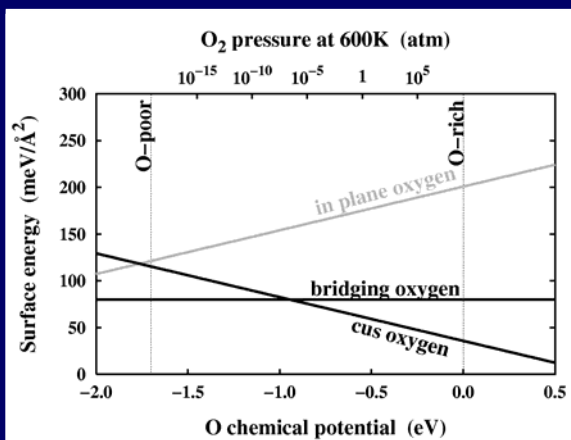
$$G(T, p) = E^{\text{tot}} + F^{\text{vib}} - TS^{\text{conf}} + pV$$

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).

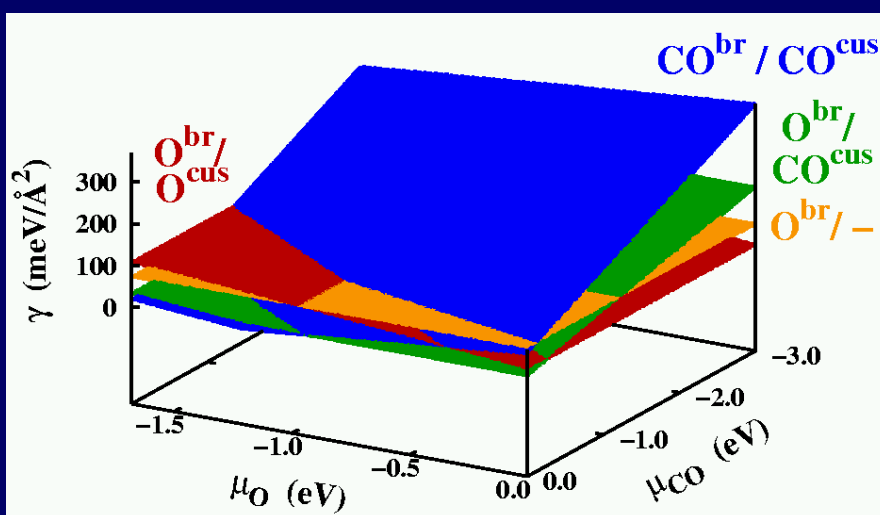
RuO₂(110) surface terminations



high pressure termination →

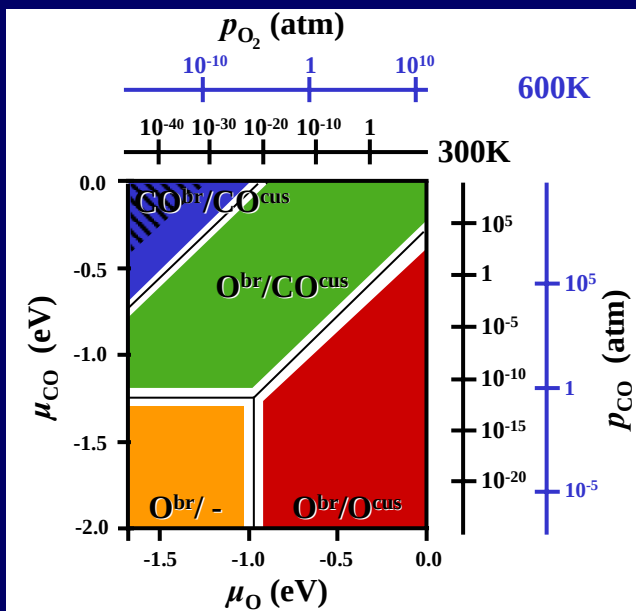
K. Reuter et al., PRB 65 (2001)

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

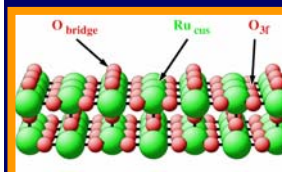


K. Reuter & M.S., PRL 90, 046103 (2003)

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



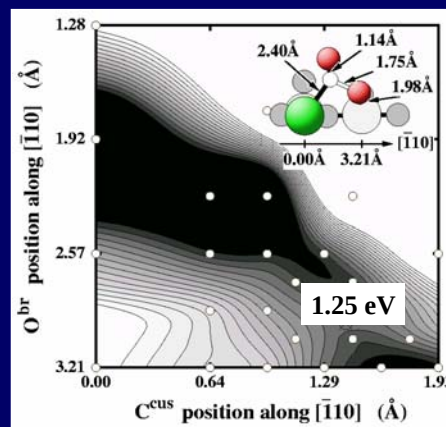
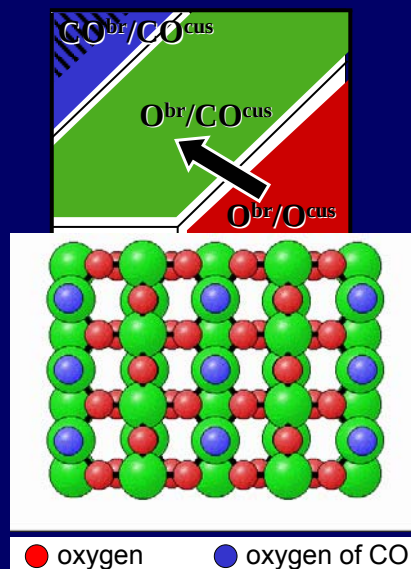
For a
“constrained
equilibrium”



UHV surface
termination

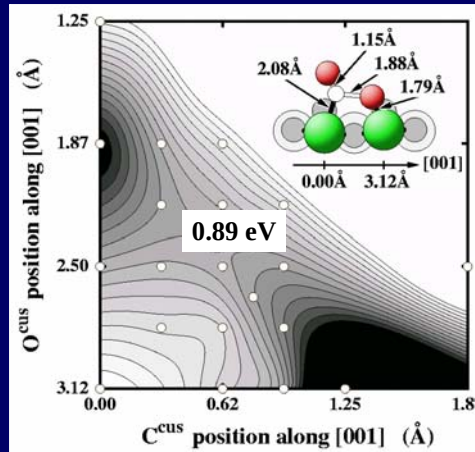
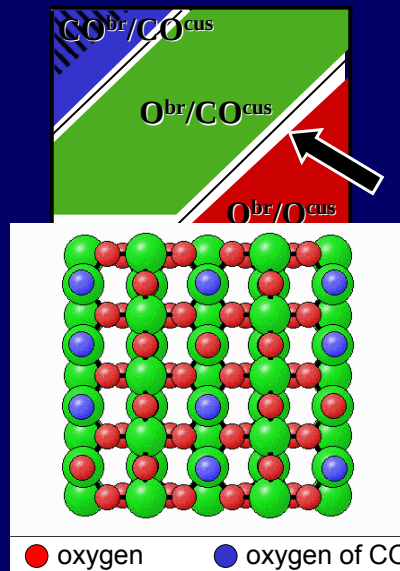
*K. Reuter & M.S.,
PRL 90, 046103 (2003)*

Possible reaction mechanisms: $\text{CO}^{\text{cus}} + \text{O}^{\text{br}} \rightarrow \text{CO}_2$



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

Possible reaction mechanisms:



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

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 (CO₂ formation)
 - desorption of the product



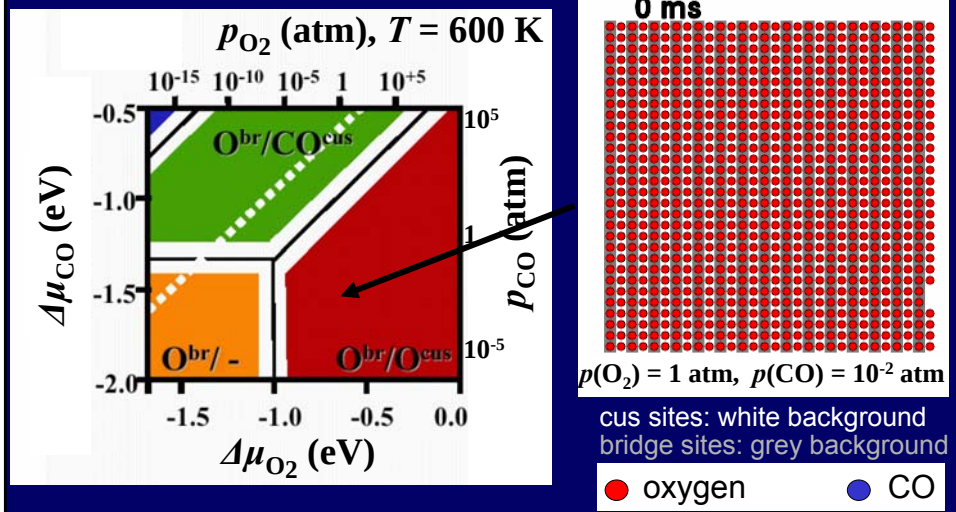
kinetic Monte Carlo method



movies

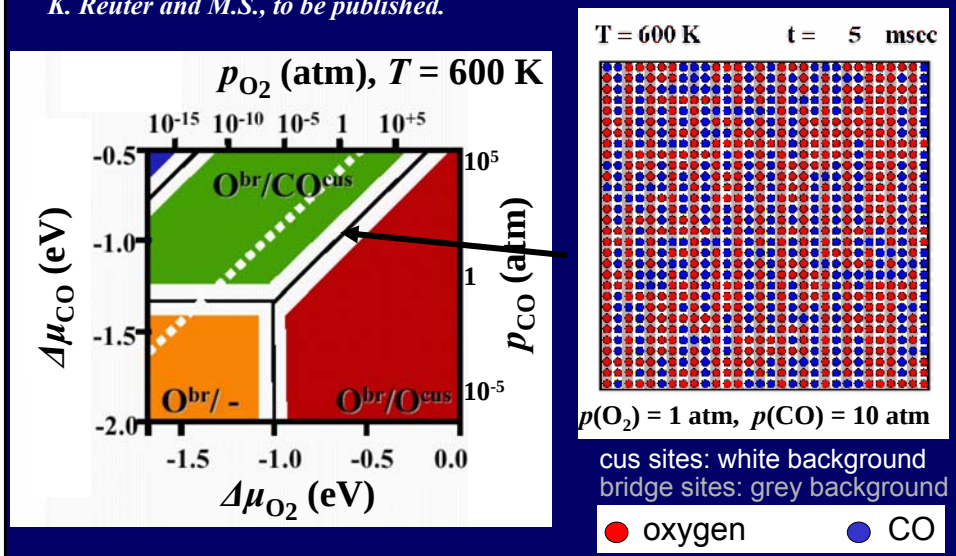
RuO₂ (110) stability regions in (T, p) space

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



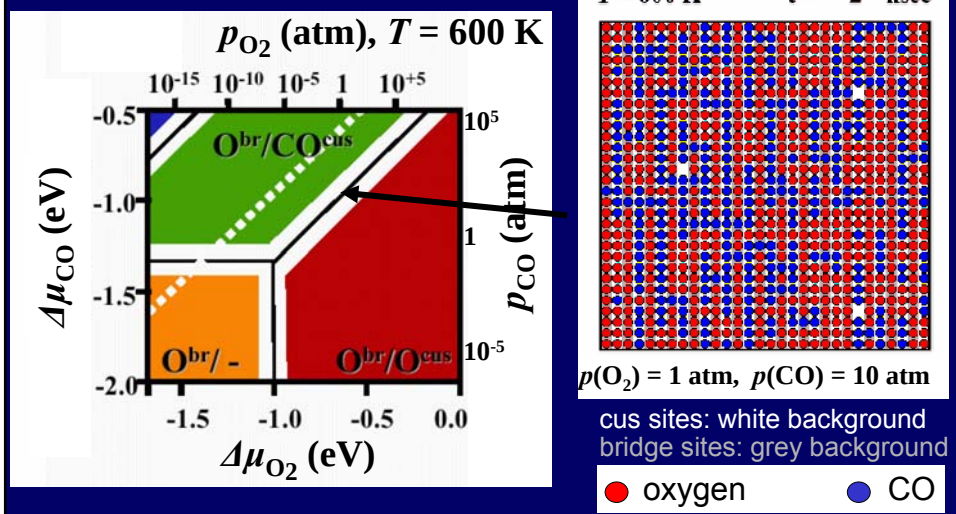
RuO₂ (110) stability regions in (T, p) space

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



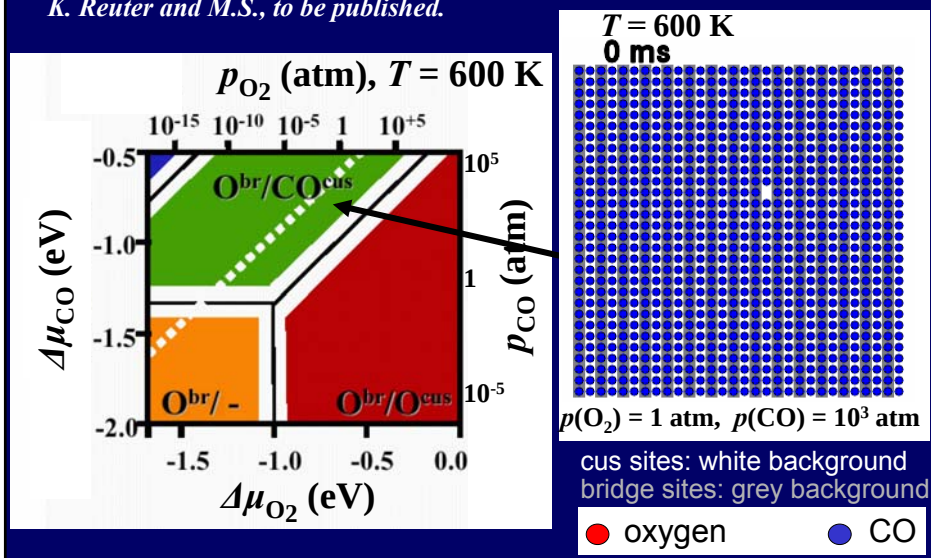
RuO₂ (110) stability regions in (T, p) space

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



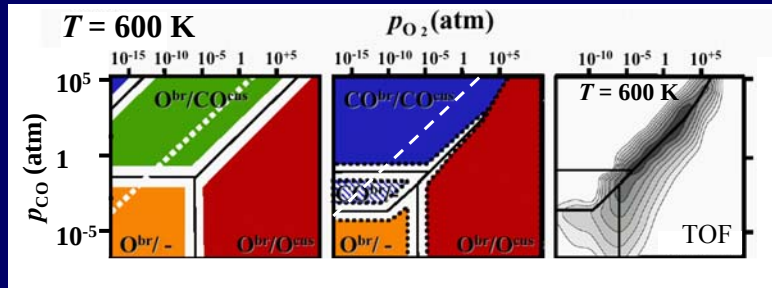
RuO₂ (110) stability regions in (T, p) space

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



RuO₂ (110) high reactivity regions

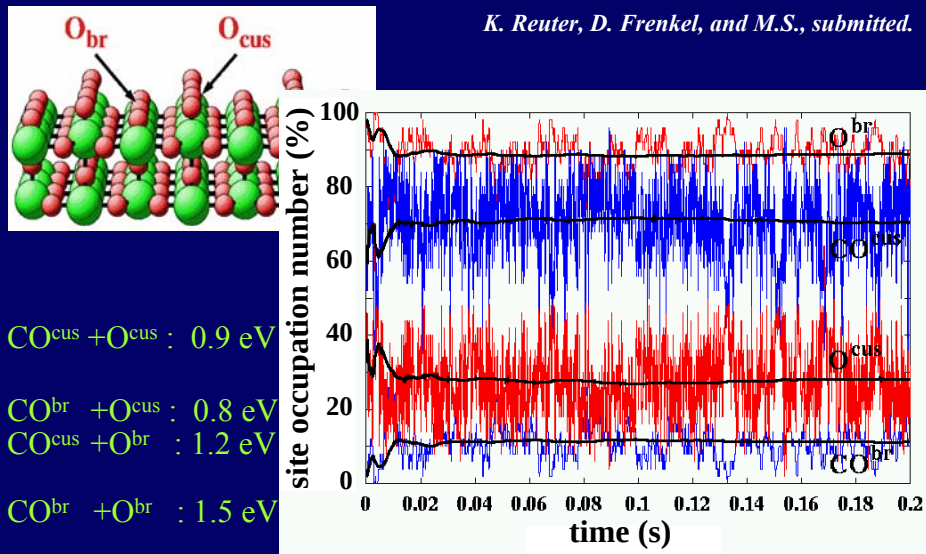
(bridging the pressure gap) *K. Reuter and M.S., to be published.*



- Most frequent: de- and adsorption of CO (mostly CO^{cus}).
- O desorbs “only” from cus sites (“only” as O_2).
- CO_2 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 $r_{CO_2} = 10^{18} \text{ cm}^{-2} \text{ s}^{-1}$.

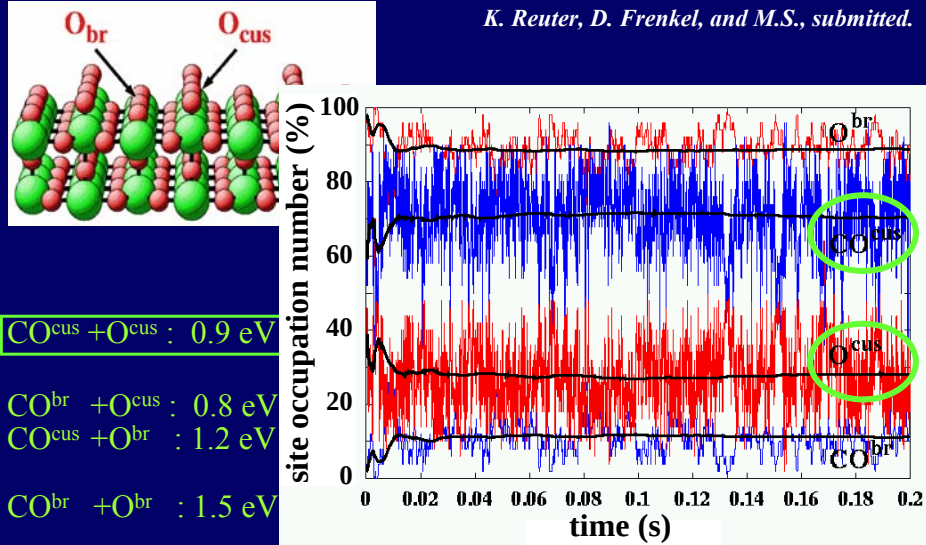
Site occupation statistics at the steady state

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



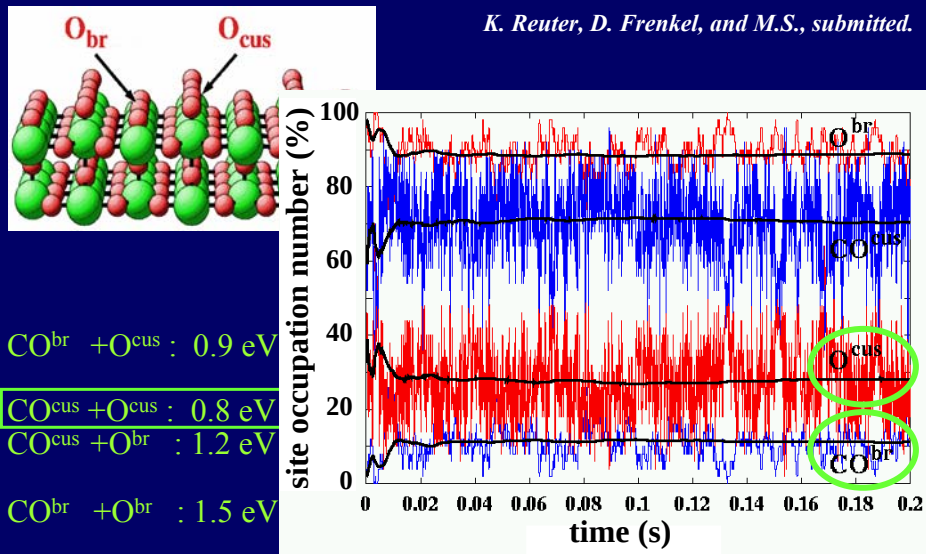
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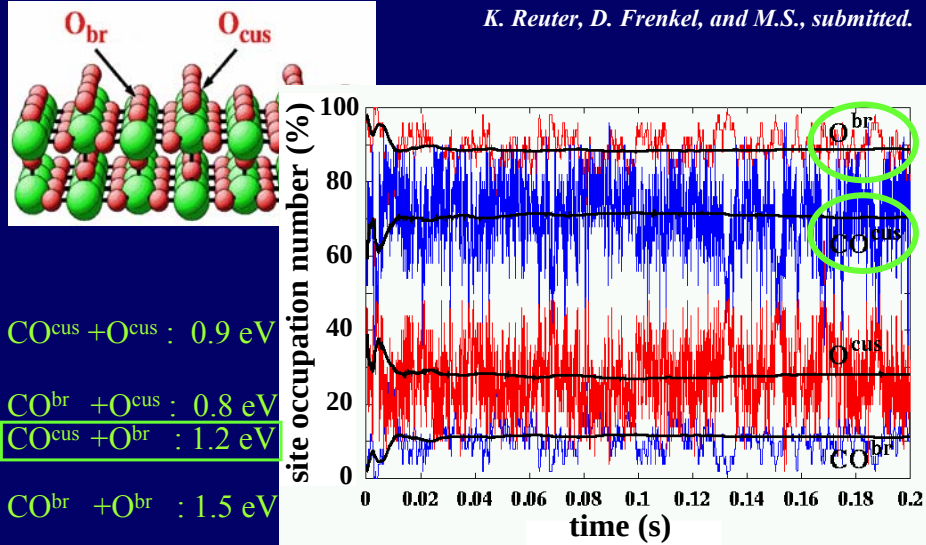
Site occupation statistics at the steady state

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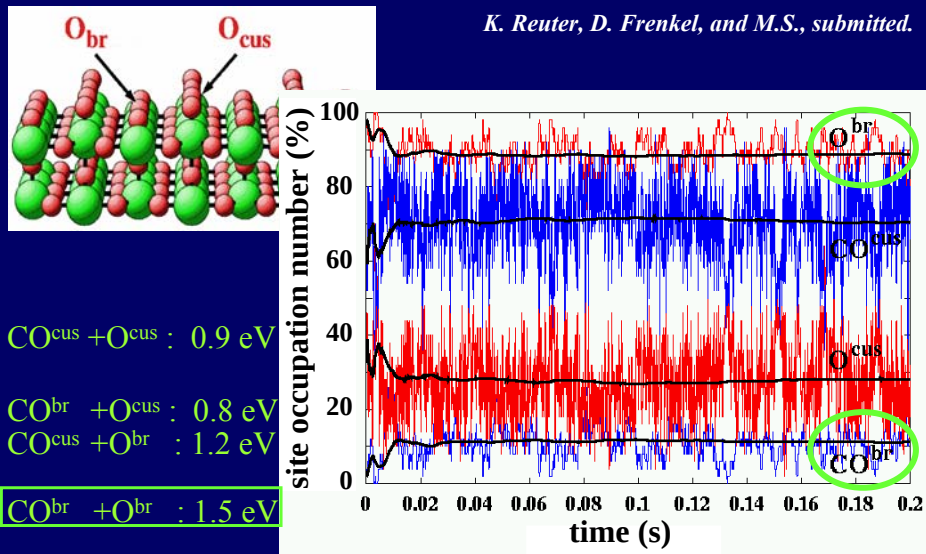
Site occupation statistics at the steady state

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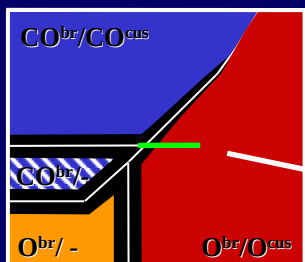


Site occupation statistics at the steady state

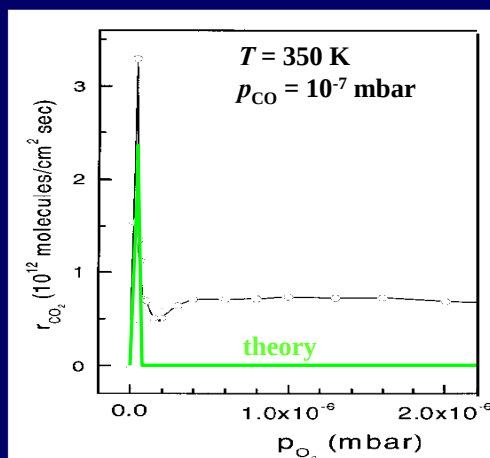
K. Reuter, D. Frenkel, and M.S., submitted.



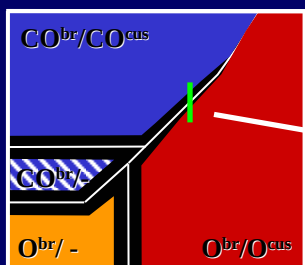
Comparison with experimental results



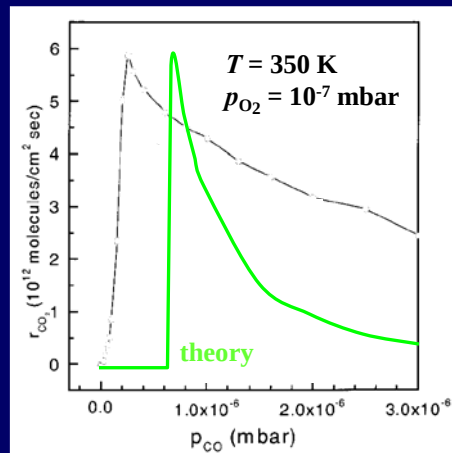
*J. Wang, C.Y. Fan,
K. Jacobi, and G. Ertl,
J. Phys. Chem. B 106,
3422 (2002)*



Comparison with experimental results

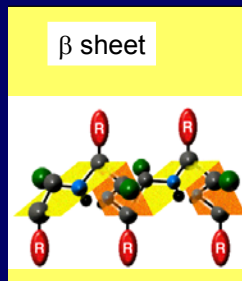
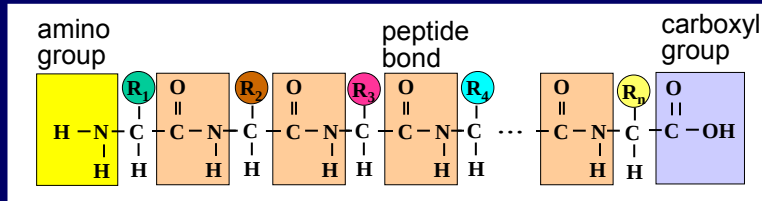
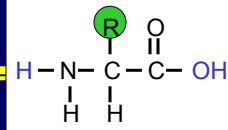


*J. Wang, C.Y. Fan,
K. Jacobi, and G. Ertl,
J. Phys. Chem. B 106,
3422 (2002)*

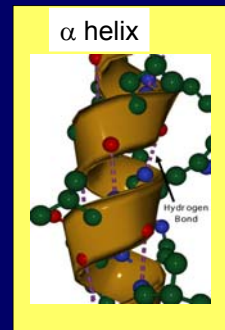


Stability of the α -helix

structure of proteins (peptide chains):

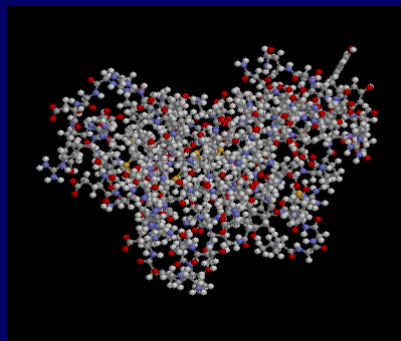


secondary structure



Folding of the peptide chain

peptide chain in the bovine prion protein



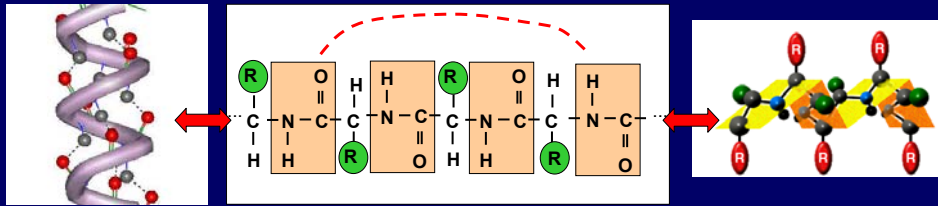
atomic structure



secondary and tertiary structure

<http://www.rcsb.org/> -- pdb-id: 1QM0

Enthalpy of formation of a hydrogen Bond



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

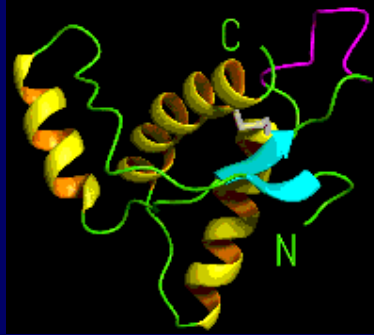
J. Ireta et al., J. Phys. Chem. B, in print.

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 QMC)

→ **Potential Energy Surface**

Dynamics of the Nuclei
along this **PES**

Thermal
Equilibrium
Structures

Statistical Mechanics

Real World

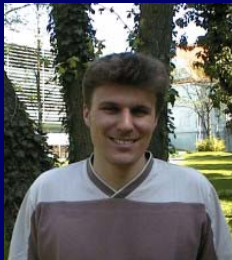
The people behind the work



Cathy Stampfl



Joel Ireta



Karsten Reuter



et al. ...



Peter Kratzer

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