united nations
educational, scientific
and cultural
organization

international atomic
energy agency

the
abdus salam
international centre for theoretical physics

ICTP 40th Anniversary

SMR 1564 - 12

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

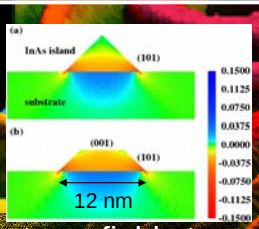
NANOMETER-SCALE PHYSICS -- THE EXAMPLES OF SEMICONDUCTOR QUANTUM DOTS AND HETEROGENEOUS CATALYSIS

Parts I - II - III

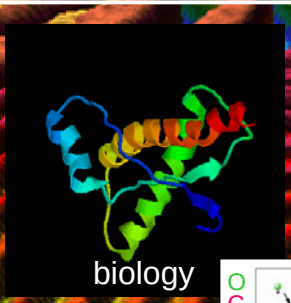
M. SCHEFFLER
Fritz-Haber-Institut der Max-Planck-Gesellschaft
Berlin, Germany

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

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

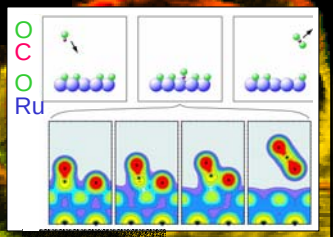


stress field at semiconductor nano structures

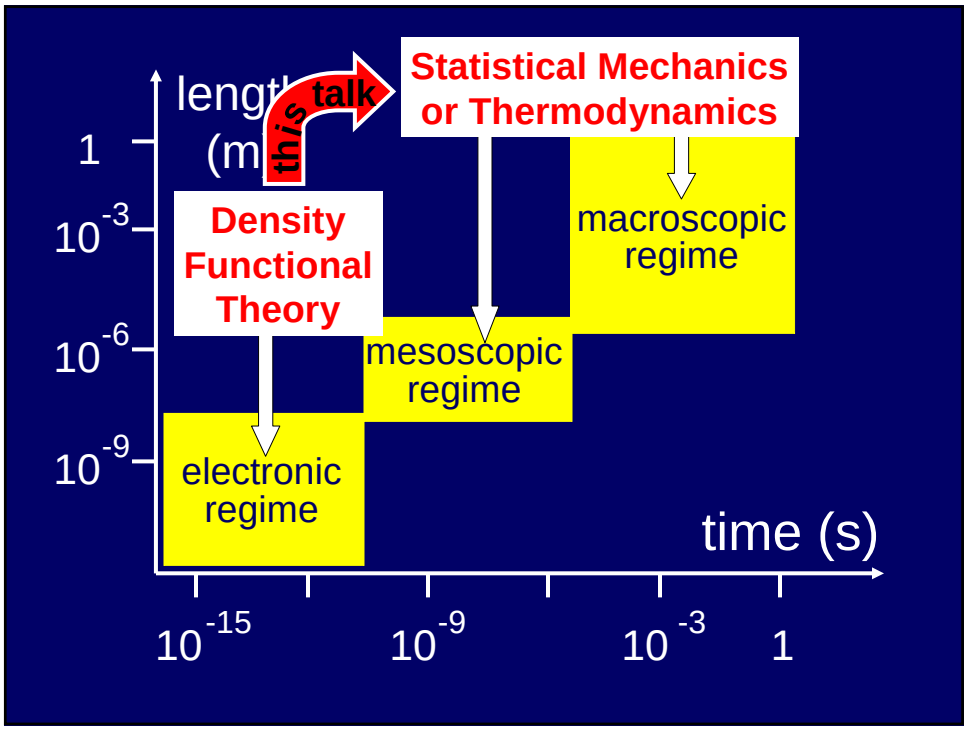


biology

electron density of adsorbates



catalysis



Density Functional Theory

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

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.*,

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

This implies:

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

Kohn and Sham (1965):

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

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].


Professor
Nkwi

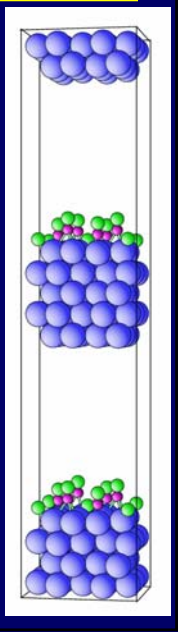
Methods

I

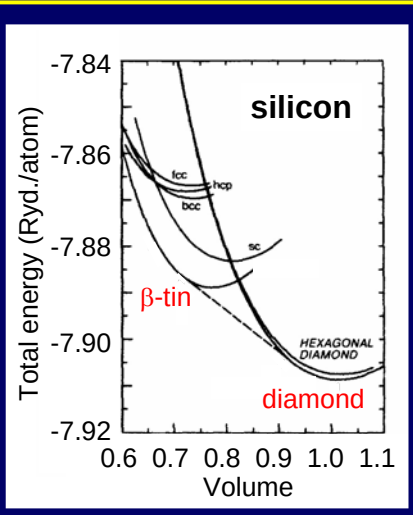
- **Density functional theory**
  - **-- *ab initio* pseudopotentials**
    (the fhi98md - code --- *www.fhi-berlin.mpg.de/th/th.html* **)**
  - **-- FP-LAPW**
    (the WIEN - code by *P. Blaha, K. Schwarz, et al.; M. Petersen et al., CPC **126** (2000)* **)**

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)*

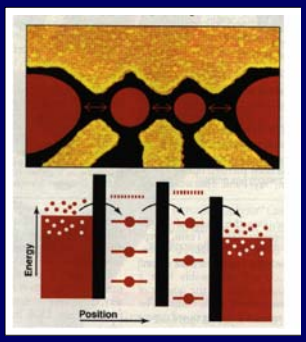
see also: V.L. Moruzzi, J.F. Janak, and A. R. Williams Calculated Electronic Properties of Metals Pergamon Press (1978)

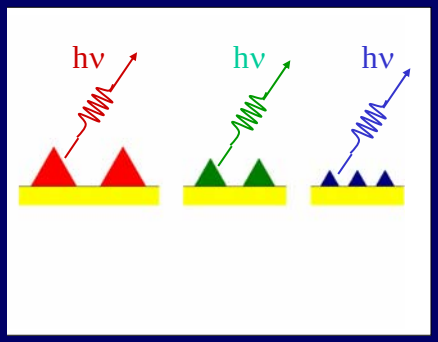
Self-Assembly of Nano-Scale Structures at Semiconductor Surfaces

Motivation:

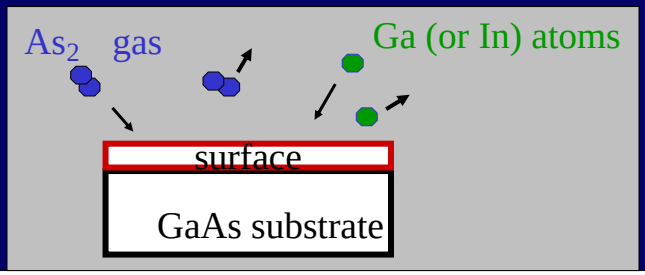
Single-electron transistor

LEDs and laser diodes





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

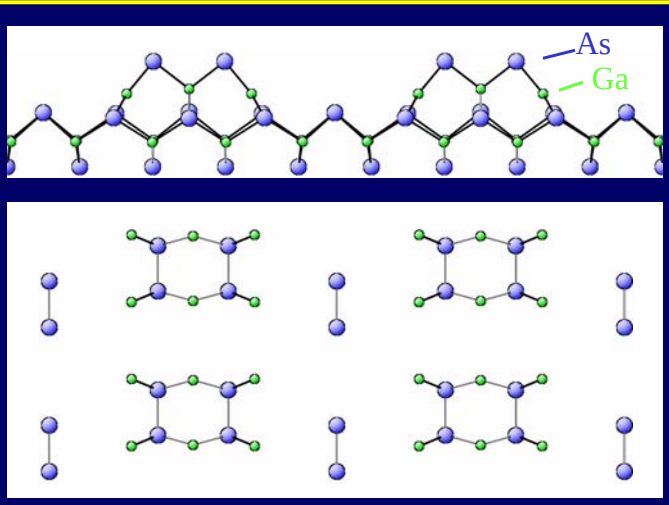


1) deposition of Ga and As
2) adsorption of Ga
3) diffusion of Ga
4) desorption of Ga
5) adsorption of As_2 ?
6) dissociation of As_2 ?
7) diffusion of As
8) desorption of As
9) island nucleation
10) growth

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

side view

top view

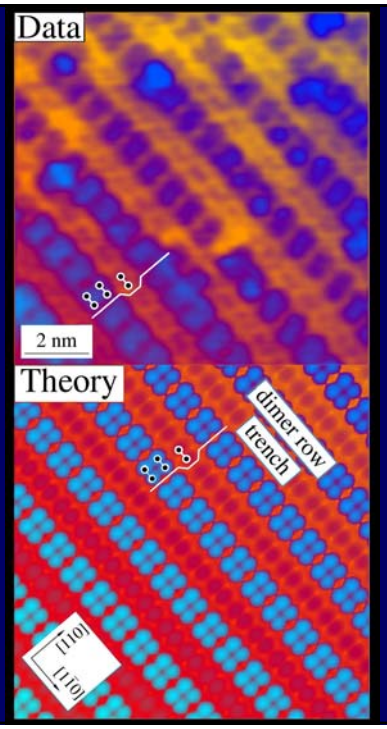


STM Imaging of GaAs(001)

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

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

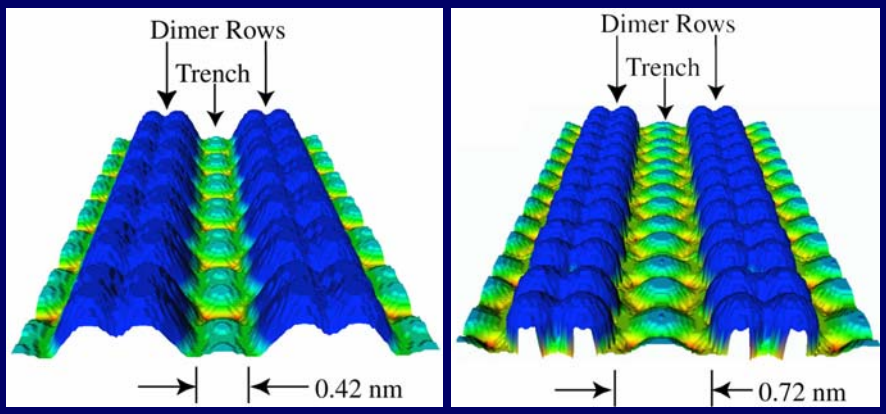
*LaBella, Yang, Bullock, Thibado, Kratzer & Scheffler, PRL **83**, 2989 (1999).*



Voltage Dependence of the STM Current

STM Simulation

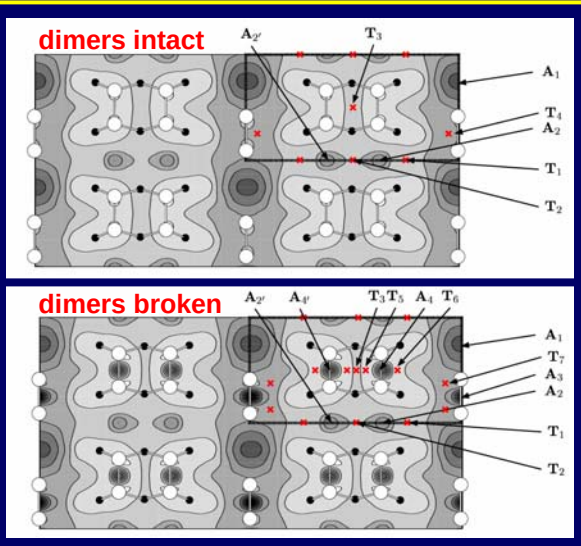
-3.0 eV (high) -2.1 eV (low)



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

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

top view



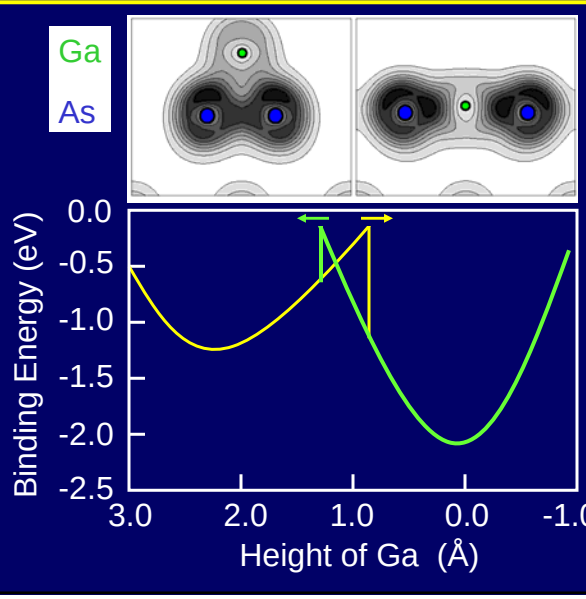
E_{A1} = -1.9 eV
E_{TS} = -1.5 eV

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)*

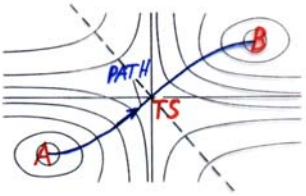
Unusually stable site for Ga adatom inside the trench-site As-dimer



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

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

Transition State Theory



Transition state theory

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

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

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

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

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

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

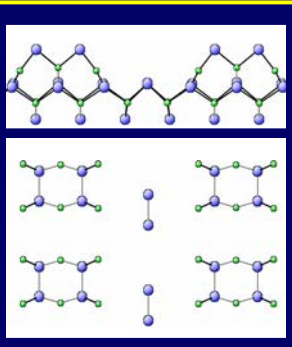
3) Statistical approach to describe
   - deposition
   - diffusion
   - nucleation
   - growth

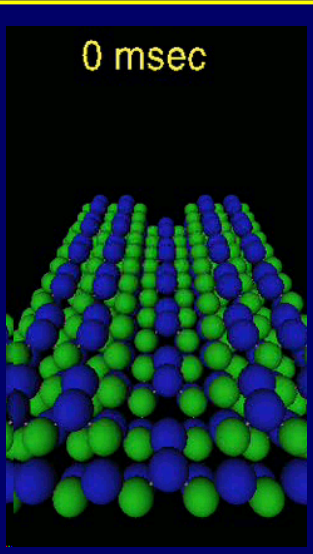
➡ **kinetic Monte Carlo method**

Adsorption, diffusion, island nucleation, and growth of GaAs

side view

top view



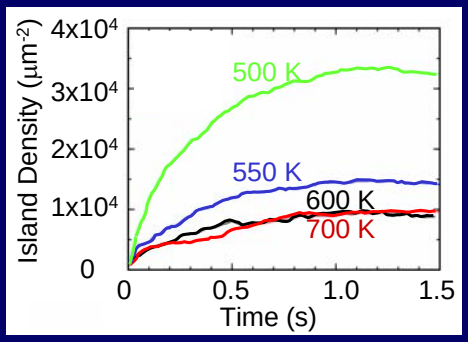


1/60 of the full simulation cell
As_2 pressure ≈ 1.33×10^{-8} bar
Ga deposition rate = 0.1 ML/s
T = 700 K

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

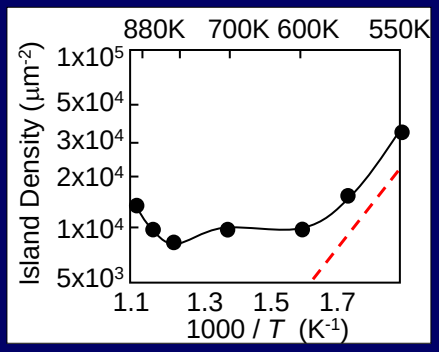
Island density

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



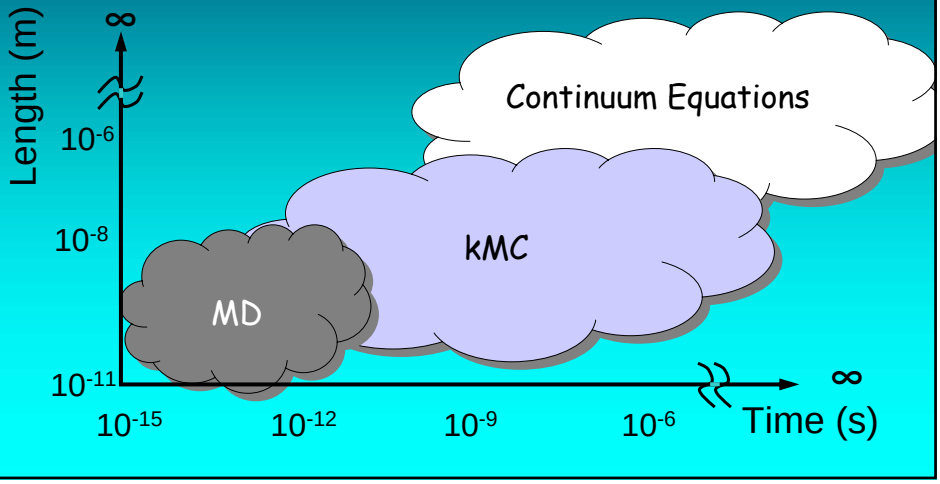
As_2 pressure
= 1.33×10^{-8} bar

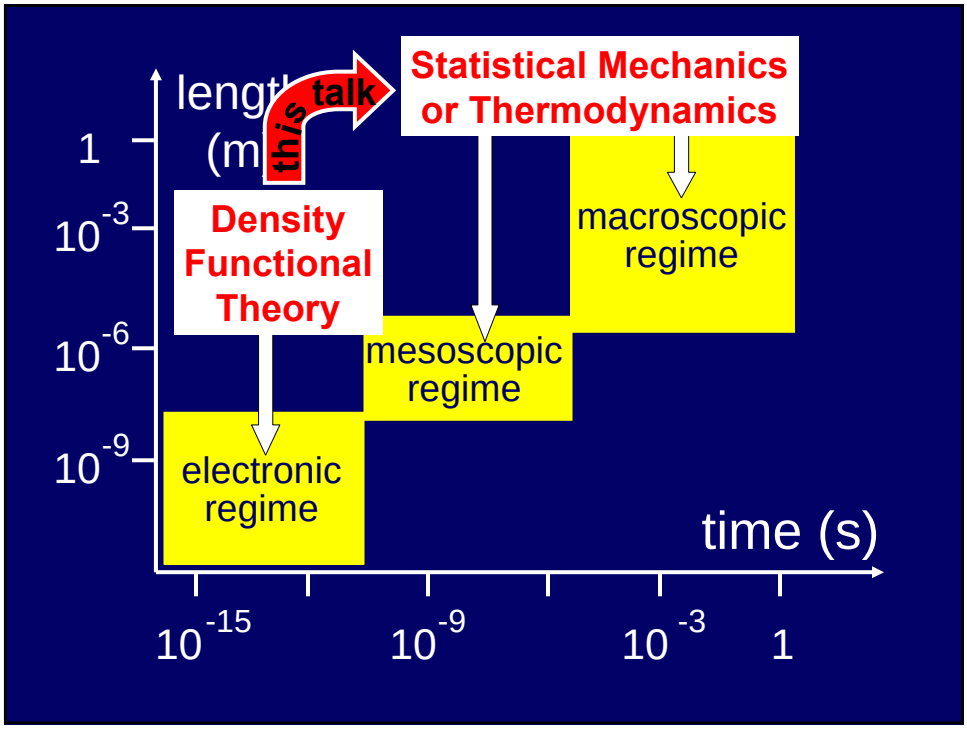
Ga deposition rate
= 0.1 ML/s

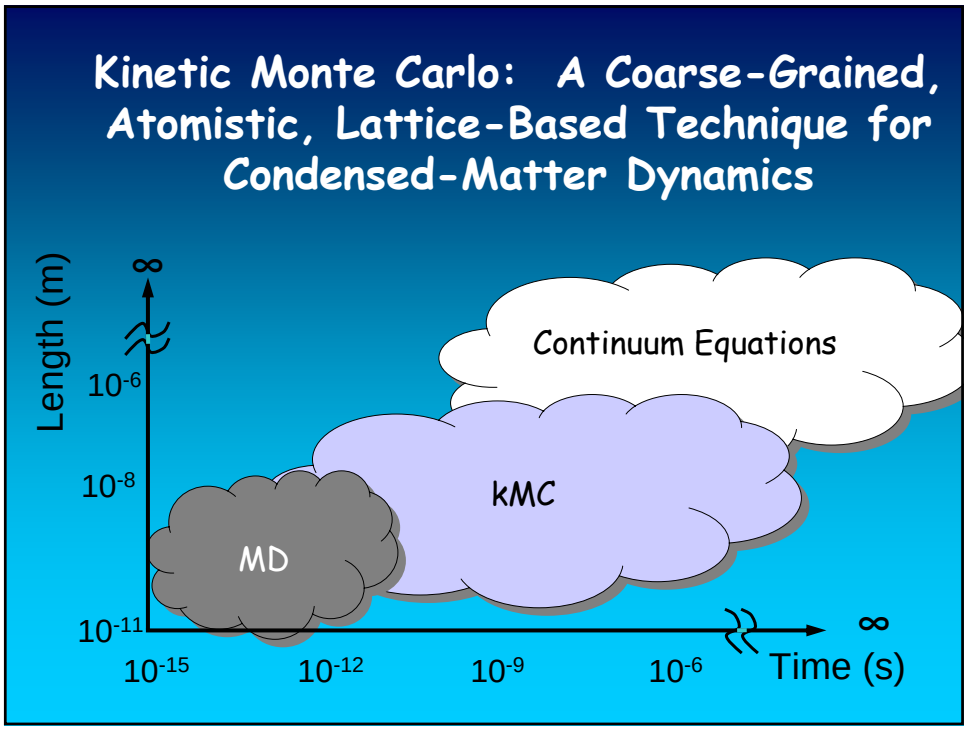


Log_{10} of island density does not increase linearly with $1/T$: Unusual *increase* of island density with increasing T (for $T > 800$ K).

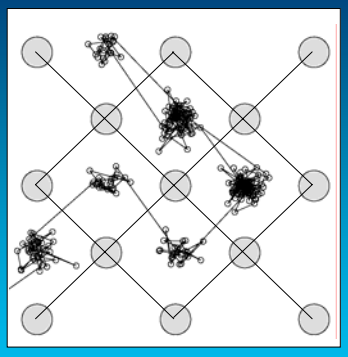
Kinetic Monte Carlo: A Coarse-Grained, Atomistic, Lattice-Based Technique for Condensed-Matter Dynamics



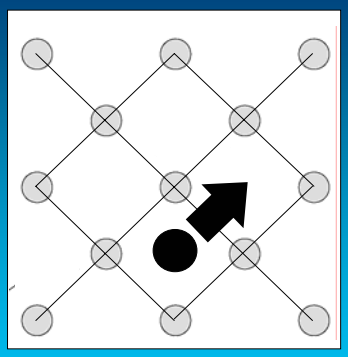

length (m)
this talk
Statistical Mechanics or Thermodynamics
1
10-3
10-6
10-9
Density Functional Theory
macroscopic regime
mesoscopic regime
electronic regime
time (s)
10-15
10-9
10-3
1


Kinetic Monte Carlo: A Coarse-Grained, Atomistic, Lattice-Based Technique for Condensed-Matter Dynamics
Length (m)
∞
10-6
10-8
10-11
Continuum Equations
kMC
MD
10-15
10-12
10-9
10-6
∞
Time (s)

Kinetic Monte Carlo: Coarse-Graining MD



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



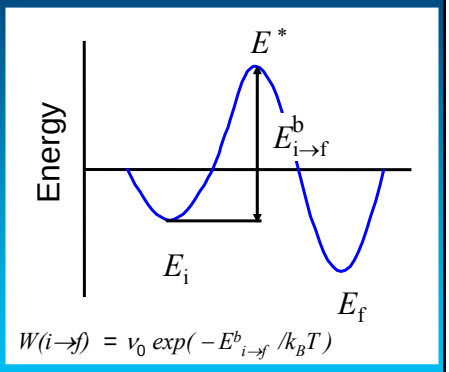
kMC: Coarse-Grained Hops

KMC Transition Probabilities and the Detailed-Balance Criterion

$$\frac{W(\vec{x}\to\vec{x}')}{W(\vec{x}'\to\vec{x})}=\exp\left[-\delta A/k_BT\right]$$

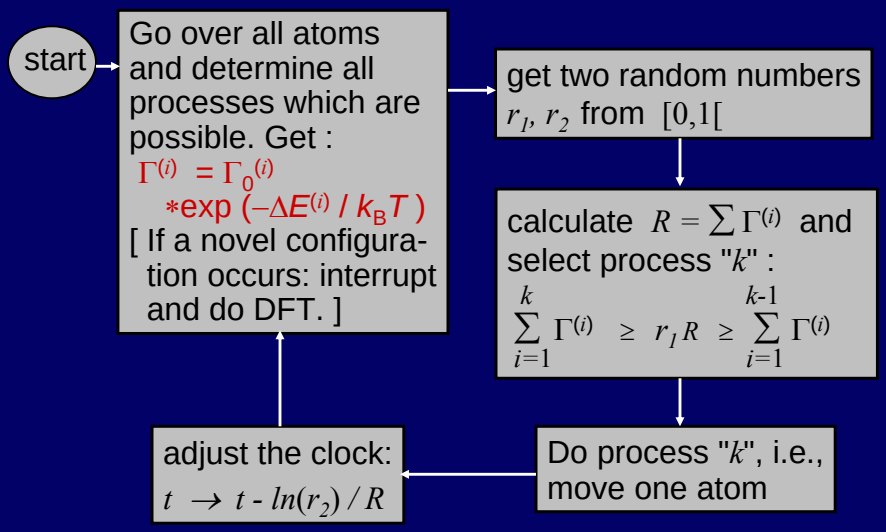
Metropolis MC Satisfies Detailed Balance, but not Kinetics

$$W(i\to f)=\begin{cases}1 & \text{if } E_f\le E_i\\ e^{-\Delta E/k_BT} & \text{if } E_f>E_i\end{cases}$$



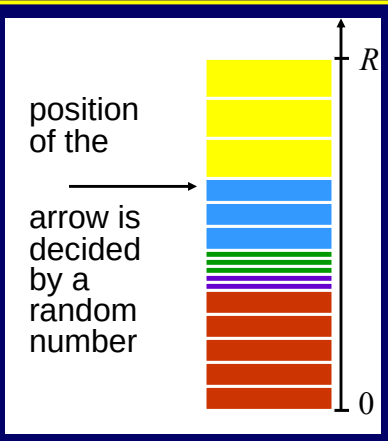
TST Satisfies Detailed Balance and Kinetics

Flowchart of kinetic Monte Carlo Simulation



unsuccessful processes are avoided

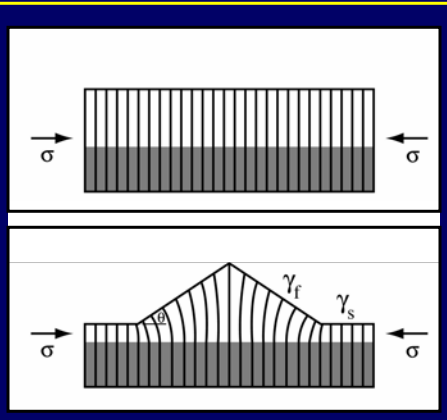
Sketch of the kMC Approach



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: As_2 adsorption into the intermediate.

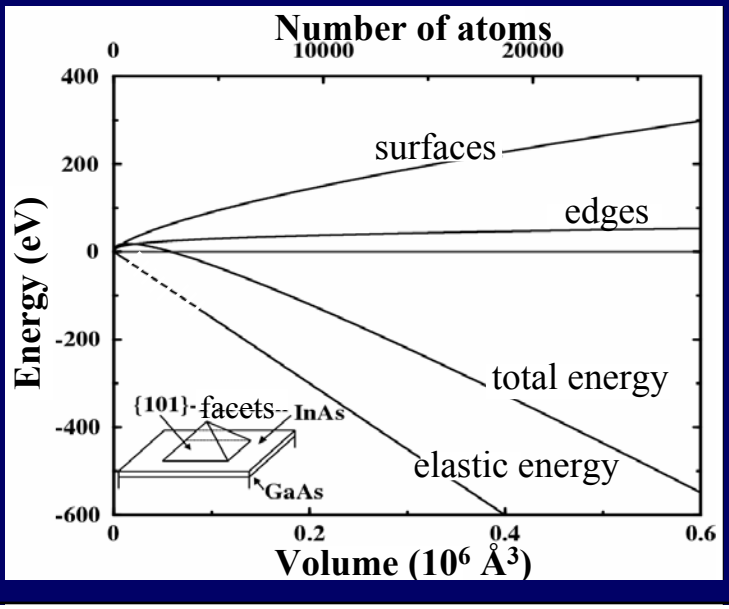
Stranski-Krastanow morphology
as one way to reduce misfit strain energy



e.g. InAs on GaAs

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

Equilibrium Shape of Quantum Dots

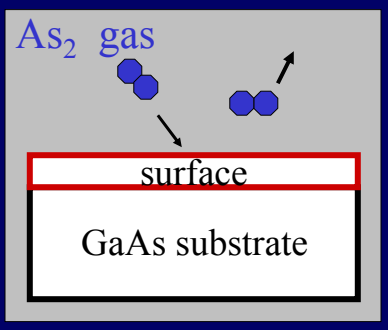


L. Wang, P. Kratzer, and M.S., PRL **82** *(1999)*

Stoichiometry and Structure of the Surface depend on the Environment

(atomic chemical potentials)

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



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

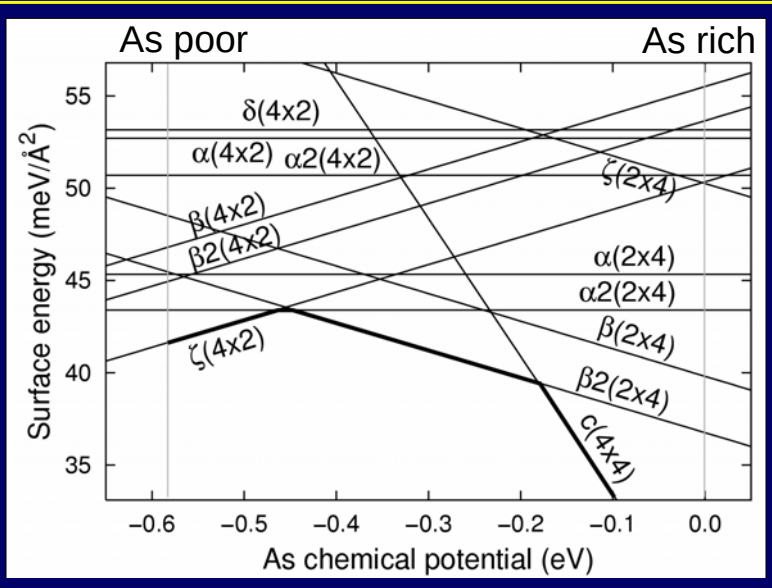
Only one independent variable:

$$\mu_{As}(T, p) = \tfrac{1}{2}\,\mu_{As_2}(T, p^0) + \tfrac{1}{2}\,kT\ln(p/p^0)$$

ab initio atomistic thermodynamics

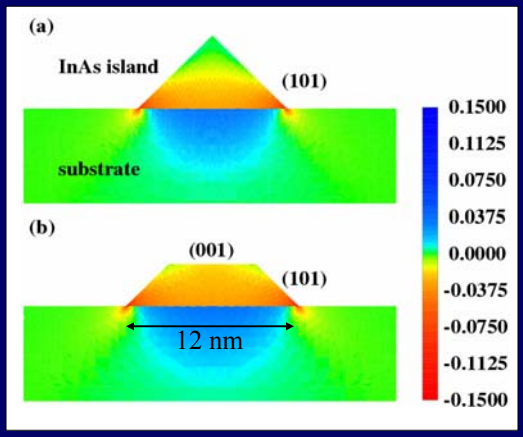
C.M. Weinert and M.S., Mat. Sci. Forum 10-12, 25 (1986).
Reuter and M. S., Phys. Rev. B 65, 035406 (2002); PRL 90, 046103 (2003).

Surface Energies of Clean GaAs (001)

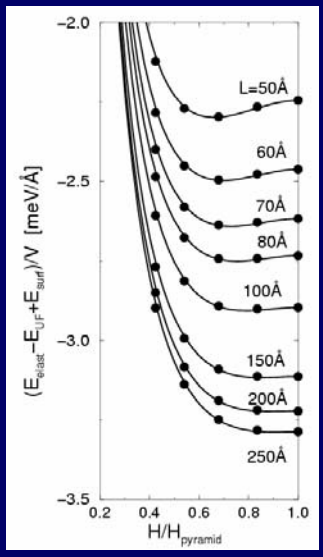


Sung-Hoon Lee, W. Moritz, & M.S., PRL 85, 3890 (2000)

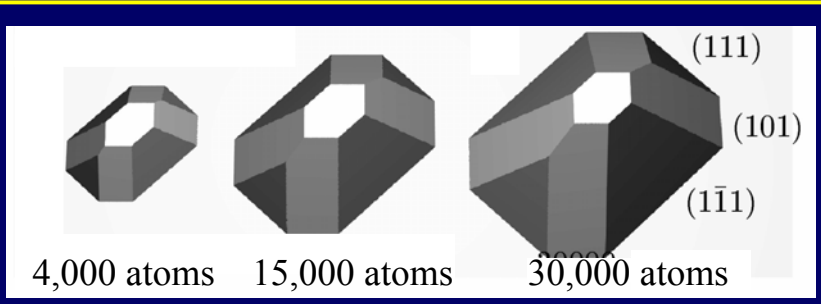
Stress Tensor at strained InAs Islands on GaAs

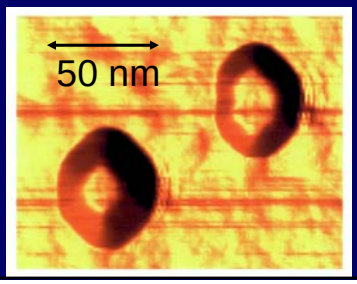


N. Moll, M.S., and E. Pehlke, PRB **58,** *4566 (1998)*



InP Quantum Dots on GaP(001)



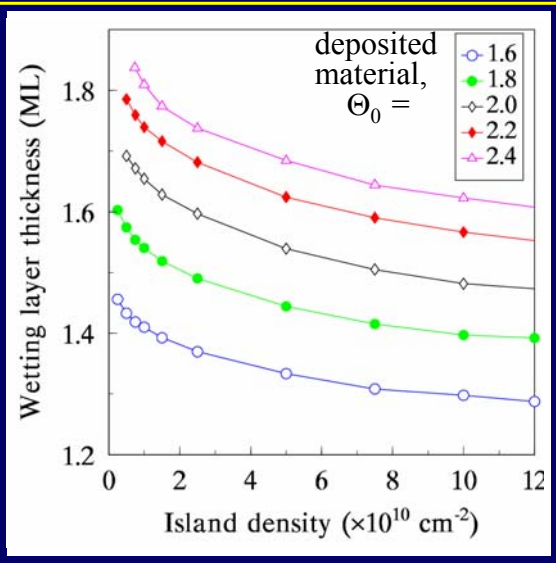


Q. Liu, E. Pehlke, N. Moll, and M.S., PRB ***60*** *(1999)*

InP islands on GaInP grown by MOVPE

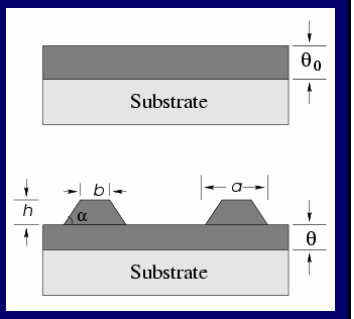
Samuelson et al. (1996)

Thickness of the Wetting Layer Depends on the Island Density



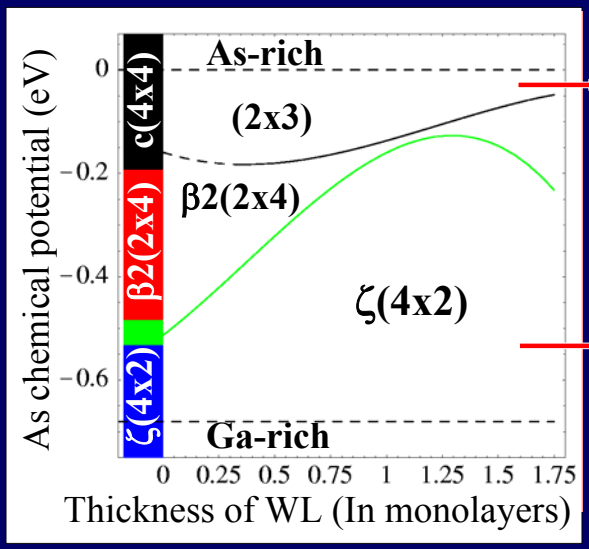
InAs on GaAs

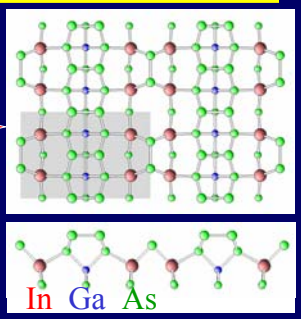
$\mu_{As} = E^{bulk}(As) - 0.2$ eV

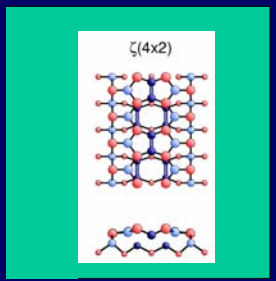


L. Wang, P. Kratzer, & M.S., PRL 82 (1999)

Reconstruction of the Wetting Layer

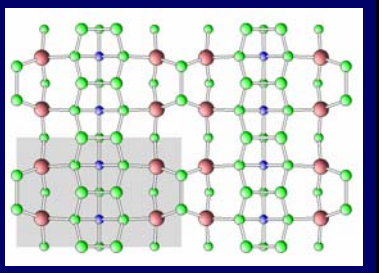






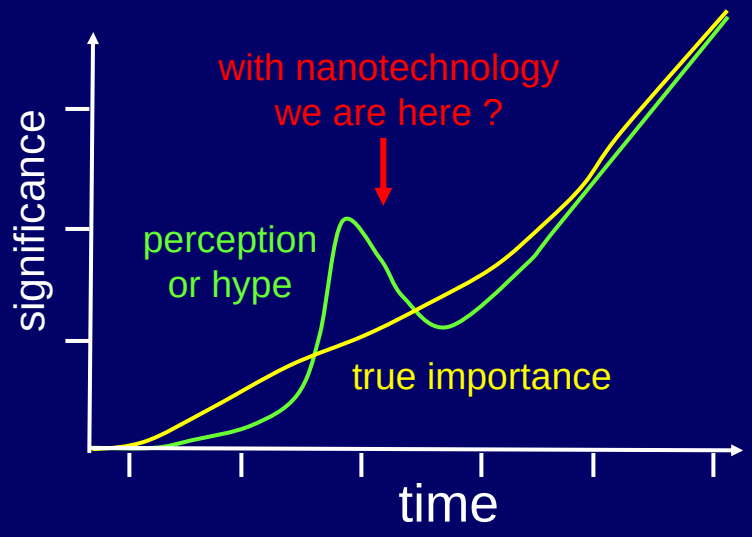
Small islands grow fast, and big (coherent) quantum dots develop a "repulsive ring"

- 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

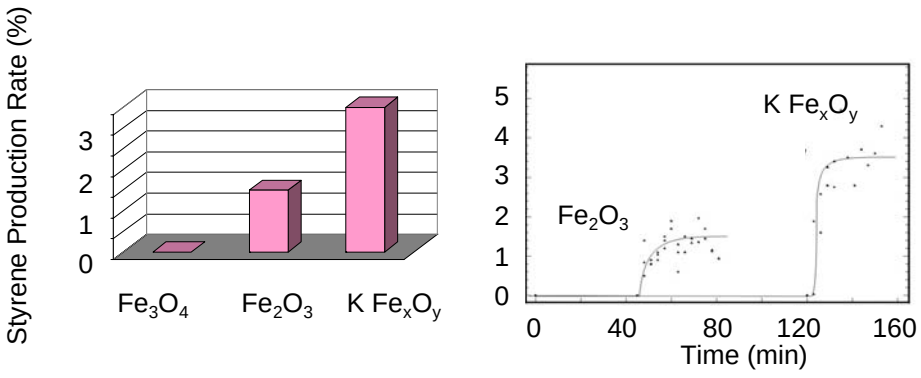
$C_6H_5CH_2CH_3 \rightleftharpoons C_6H_5CH{=}CH_2 + H_2$

$(\Delta H^0_{298} = 124.9\ \text{kJ/mol})$

Parameters of the commercial process:

- reaction temperature: 580-640°C
- pressure: atmospheric
- component of feed gas: H_2O / EB = 6 / 9
- selectivity to styrene: 95%

Catalytic Activity

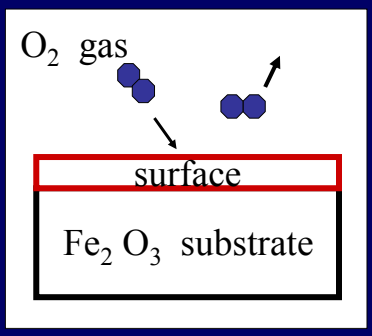


Christian Kuhrs, Modellkatalyse, Abt. AC, Fritz-Haber-Institut (MPG), Berlin

Stoichiometry and Structure of the Surface depend on the Environment

(atomic chemical potentials)

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



$$2\,\mu_{Fe} + 3\,\mu_O = E^{\text{bulk}}(Fe_2O_3)$$

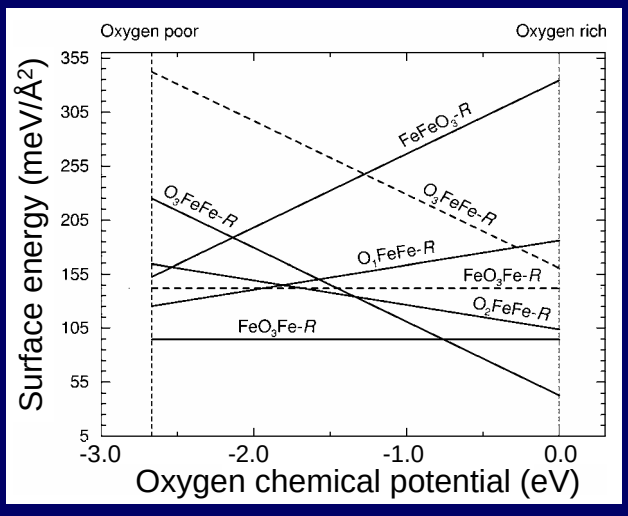
Only one independent variable:

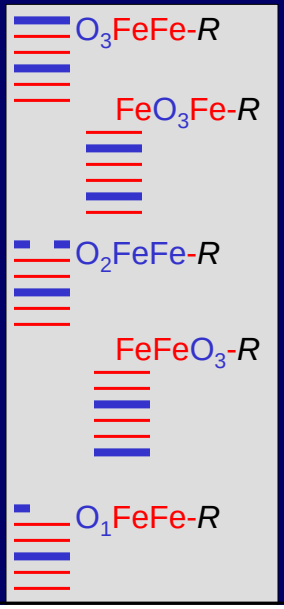
$$\mu_O (T, p) =$$

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

ab initio atomistic thermodynamics

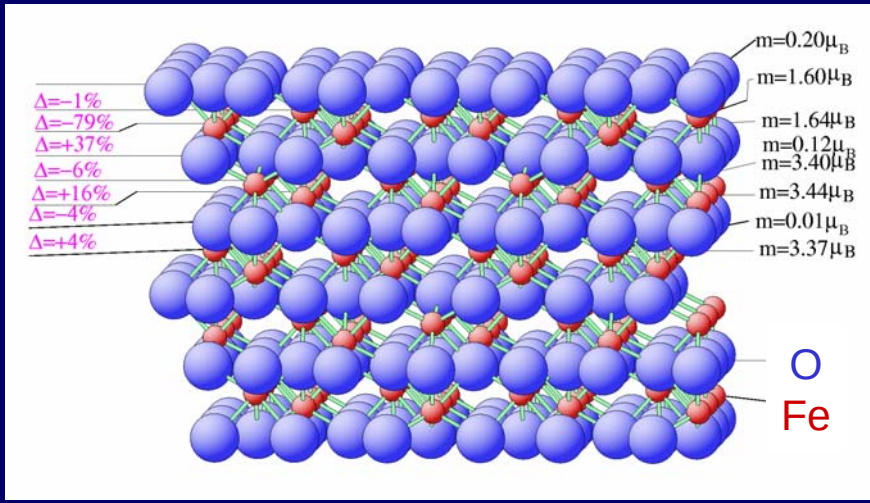
Fe_2O_3 (0001) Surface Terminations





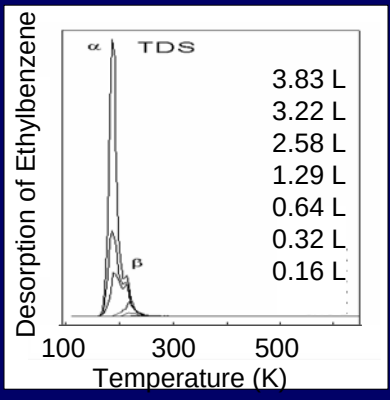
X.G. Wang et al., PRL 81 (1998)

Fe_2O_3 (0001) O-terminated Surface



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

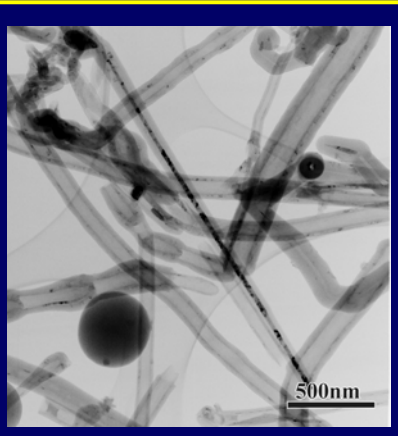
What is the active catalyst ?

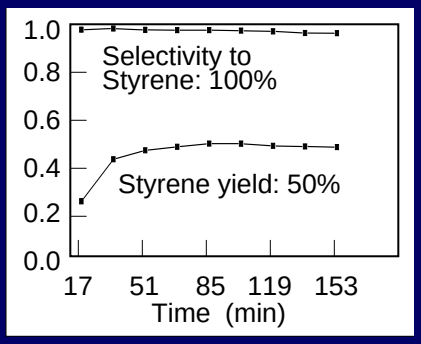


C. Kuhrs and R. Schlögl, to be published

- 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?

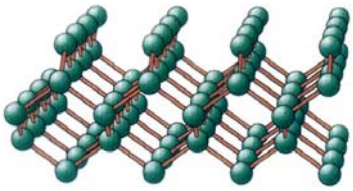
- Properties that are given by ensemble averages or ruled by the statistical interplay of many processes are well described by DFT-GGA.
- Errors in total energies can be noticeable. Even for energy *differences* they can be as large as several tenths of an eV. And sometimes this is indeed crucial.

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

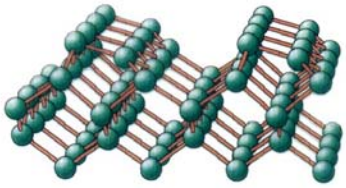
Improving the accuracy of the xc energy
(exploiting the nearsightedness)
-- local correction of the xc energy --

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

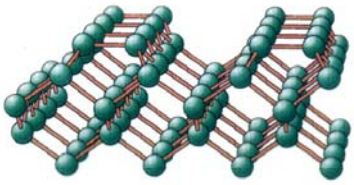
Dimerization and dimer buckling at Si(001)



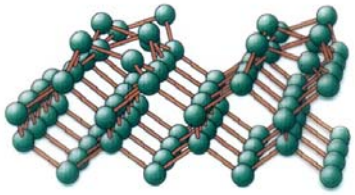
truncated bulk geometry



dimer buckling



formation of dimers

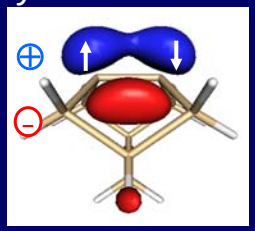


alternating buckling

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

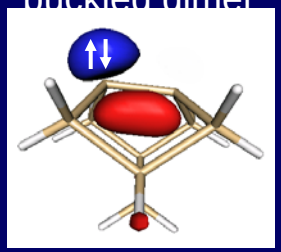
"A negative U system" ?

HOMO of symmetric dimer



Which configuration is the ground state ?

HOMO of buckled dimer

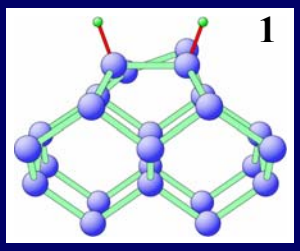


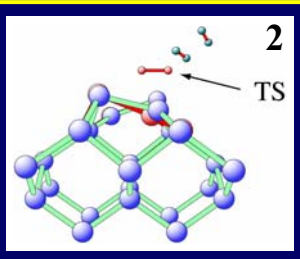
favored by MCSCF (clusters)

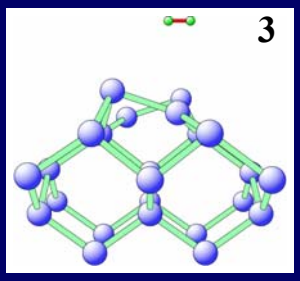
this one

favored by DFT (slabs)

The H_2 / Si(001) energy barrier puzzle

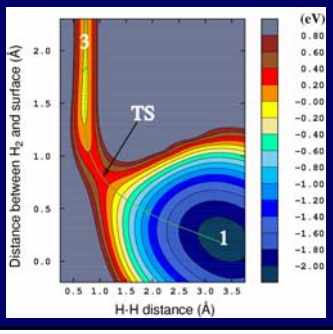




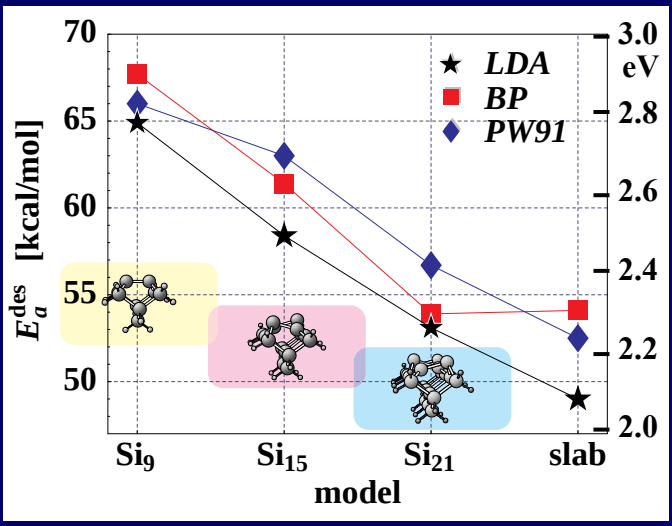


- CI-cluster and DFT-slab calculations give very different descriptions.
- Neither of them agrees with experiment.

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



Cluster models: H_2 dissociative adsorption



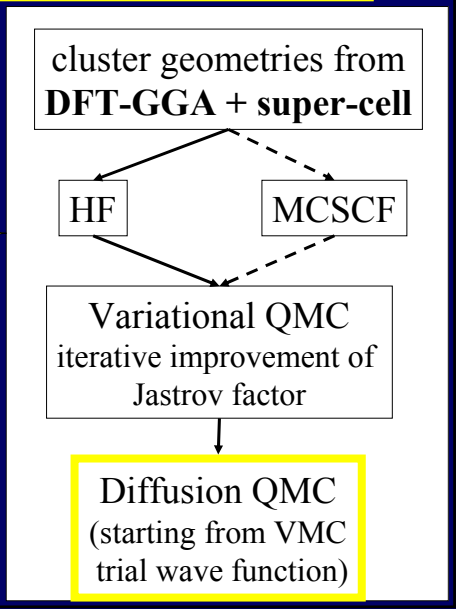
Convergence with cluster size is slow.

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

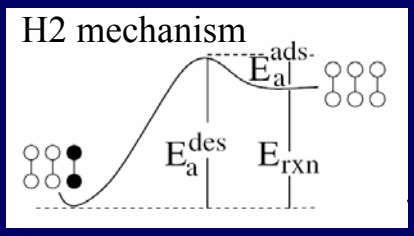
Exploiting the Nearsightedness

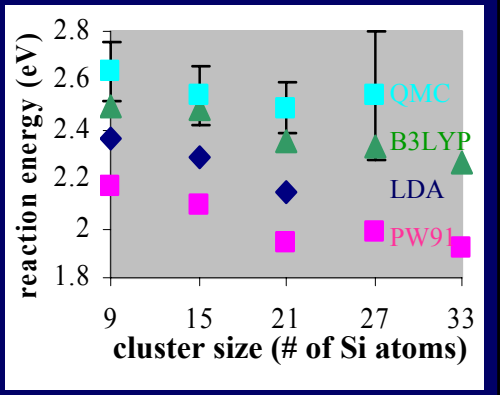
- DFT-GGA super-cell calculations
- Cluster calculations with DFT-GGA and with QMC
- Correction of the DFT-GGA exchange-correlation energy:
  $\Delta E = E_{cluster}(QMC) - E_{cluster}(GGA)$

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



Correction of the xc Energy

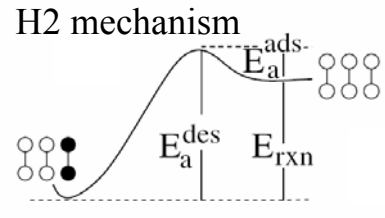




$\Delta E = E_{cluster}(QMC) - E_{cluster}(GGA) = 0.48 \pm 0.1$ eV

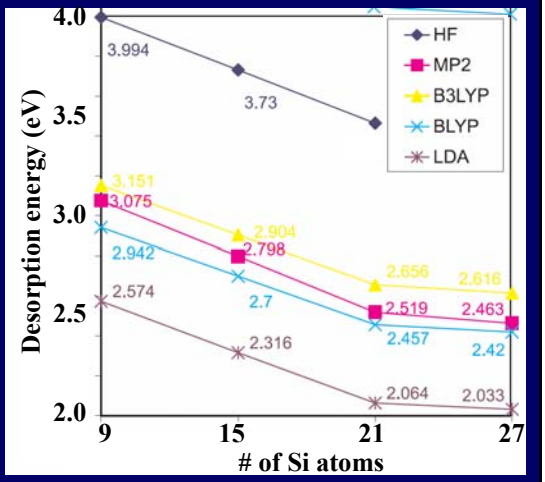
C. Filippi, S.B. Healy, P. Kratzer, E. Pehlke, and M. S., PRL 89, 166102 (2002).

Checking the quality of the xc treatment



- The total energy is nearsighted, but not much:

  Convergence with cluster size is slow.
- $\Delta E = E^{\mathrm{WF}} - E^{\mathrm{DFT\text{-}LDA}}$ 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 $E_{xc}^{..A}[n]$ 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 $T_s[n]$).

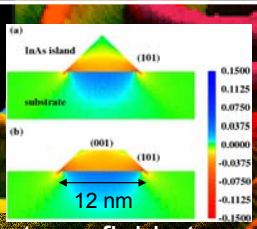
The many-body wave function, Ψ_0 , is a functional of the density, as is the many-body Hamiltonian.

Conclusions

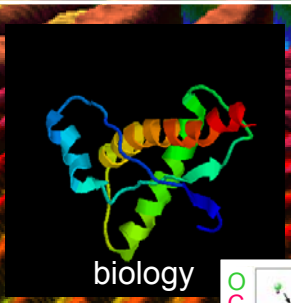
- Combining DFT and Statistical Mechanics or Thermodynamics is essential for understanding the function of materials.
- The accuracy of the method is (even) better than its reputation (compensation of DFT-LDA/GGA errors due to the statistical interplay of many processes).
- The described techniques are 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} :

$$\Delta E^{xc} = E^{\mathrm{WF}}_{\mathrm{cluster}} - E^{\mathrm{DFT\text{-}LDA}}_{\mathrm{cluster}}$$

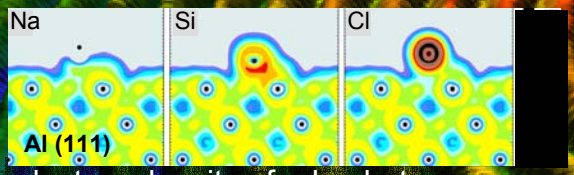
Nanometer-scale physics -- the examples of semiconductor quantum dots and heterogeneous catalysis



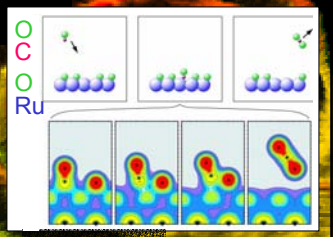
stress field at semiconductor nano structures



biology

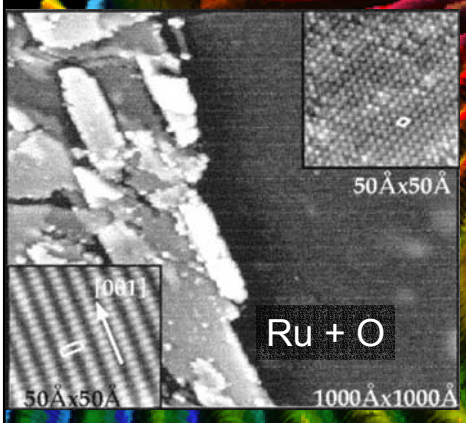


electron density of adsorbates

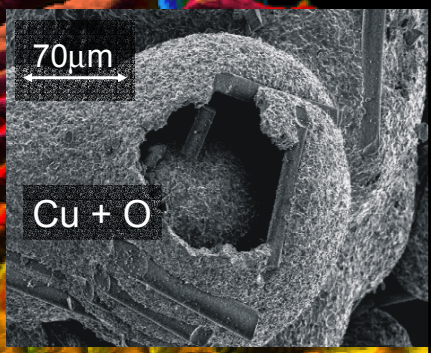


catalysis

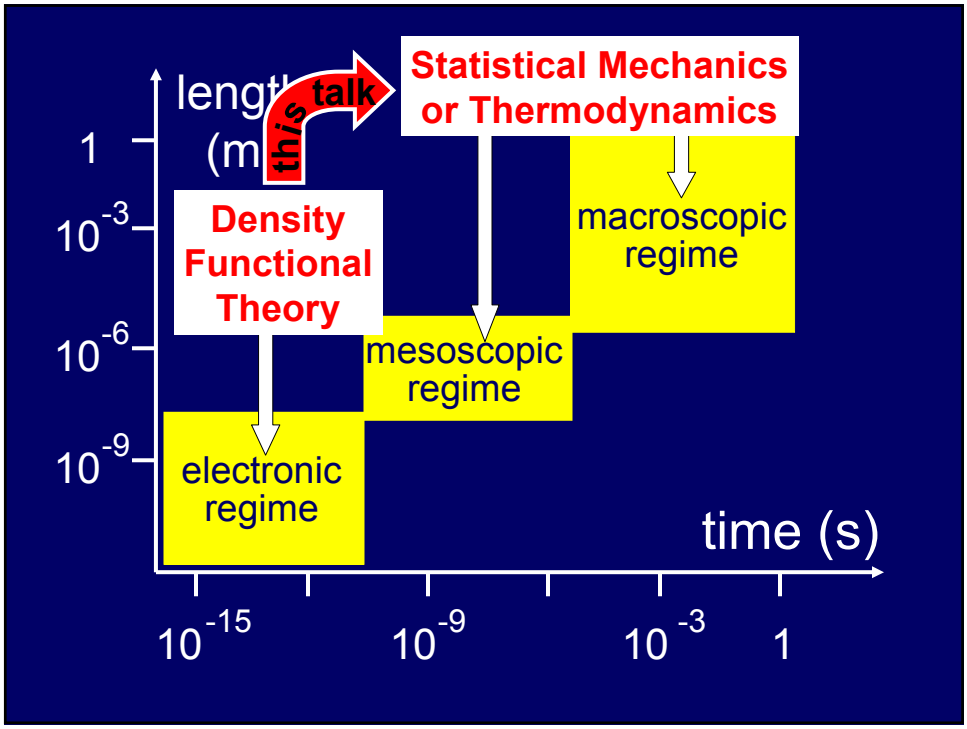
Nanometer-scale physics -- the examples of semiconductor quantum dots and heterogeneous catalysis



Ru + O



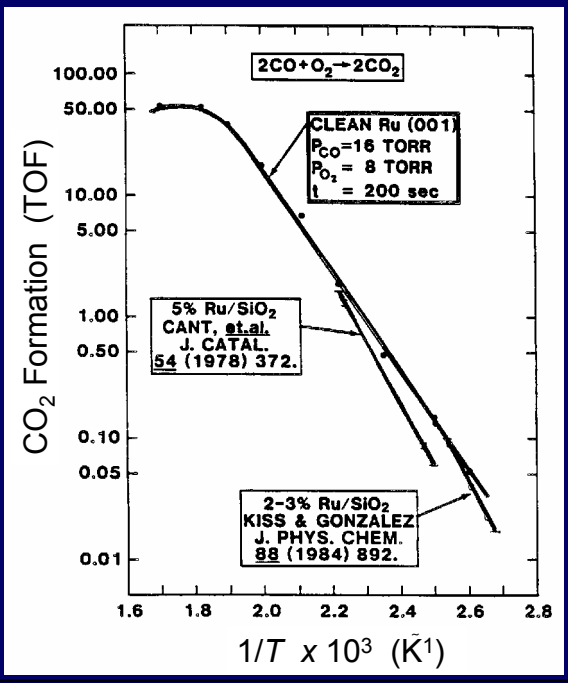
Cu + O



Oxidation catalysis, e.g.:

$$CO + \tfrac{1}{2}\, O_2 \rightarrow CO_2$$

A "simple", prototypical surface chemical reaction

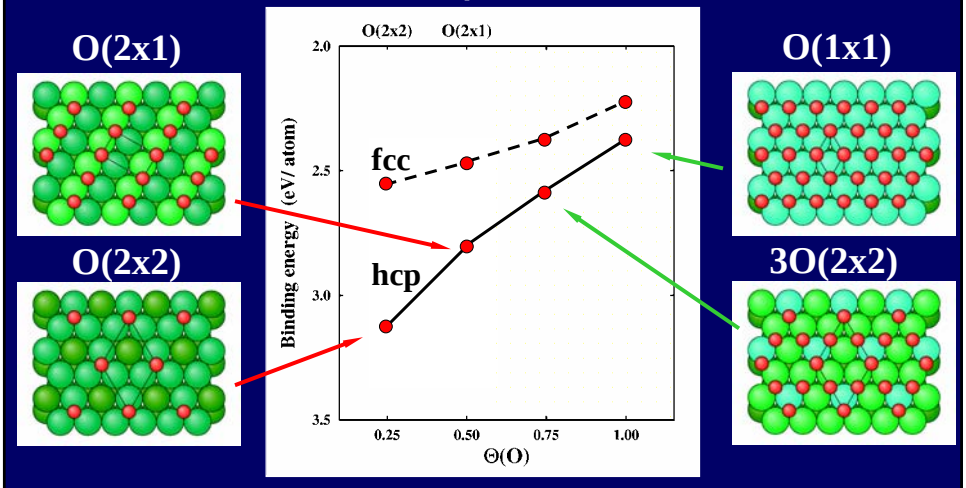


CO_2 formation at Ru supported catalysts and Ru single crystals.

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

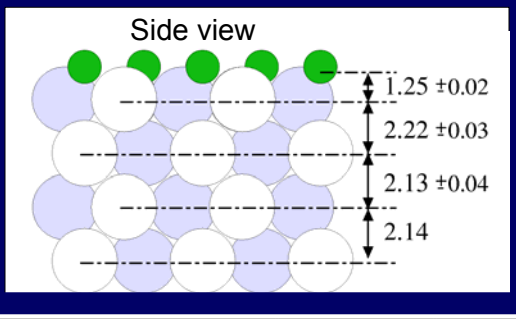
Oxygen Adsorption on Ru(0001)

UHV ▪▪▪► | High pressure



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

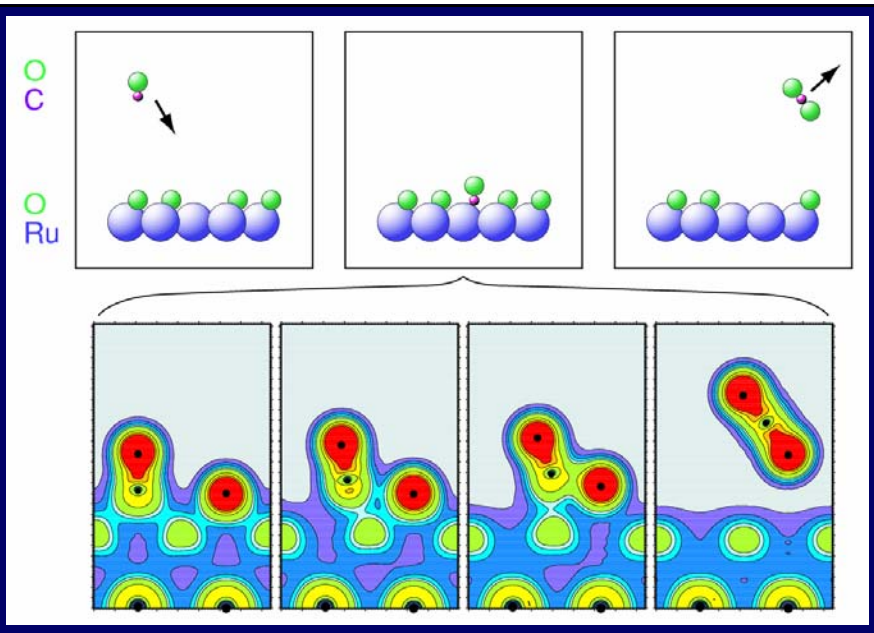
Prediction of new (unexpected) structures. Example: (1x1)-O/Ru(0001)



Prepared by O_2 adsorption up to 1/2ML, (2x1) phase, then NO_2 exposure at 600K to form 1ML (1x1) phase.

PARAMETER	DFT-GGA	LEED
Ru-O spacing (A)	1.26	1.25± 0.02
Ru-O bond length (A)	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)

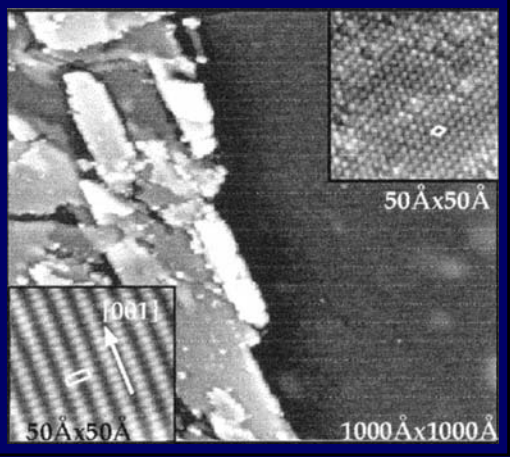


C. Stampfl, M.Scheffler, Surf. Sci. 433-435, 119 (1999), M. Scheffler and C. Stampfl, in Handbook of Surface Science (2000)

Transition-metals oxides as oxidation catalysts ? !

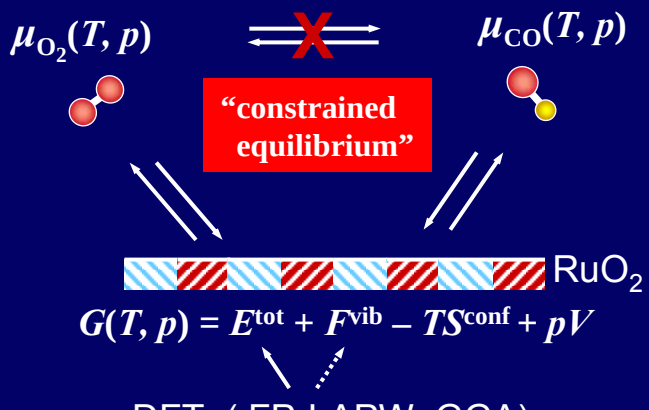
Catalytic activity of Ru(0001) is due to RuO_2(110) domains (1-2 nm thin films), that form in the re-active environment.

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



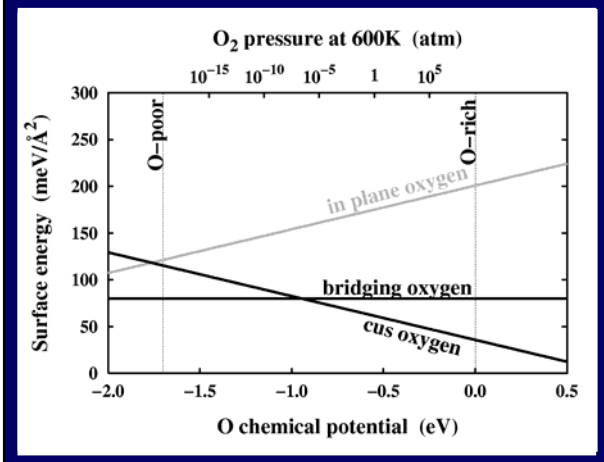
$$G(T, p) = E^{tot} + F^{vib} - TS^{conf} + pV$$

DFT (FP-LAPW; GGA)

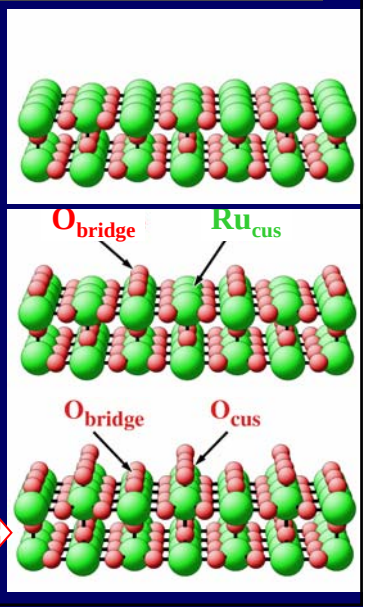
$$\mu_O(T, p) = \tfrac{1}{2}\,\mu_{O_2}(T, p^0) + \tfrac{1}{2}\,kT \ln(p/p^0)$$

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

RuO_2(110) surface terminations

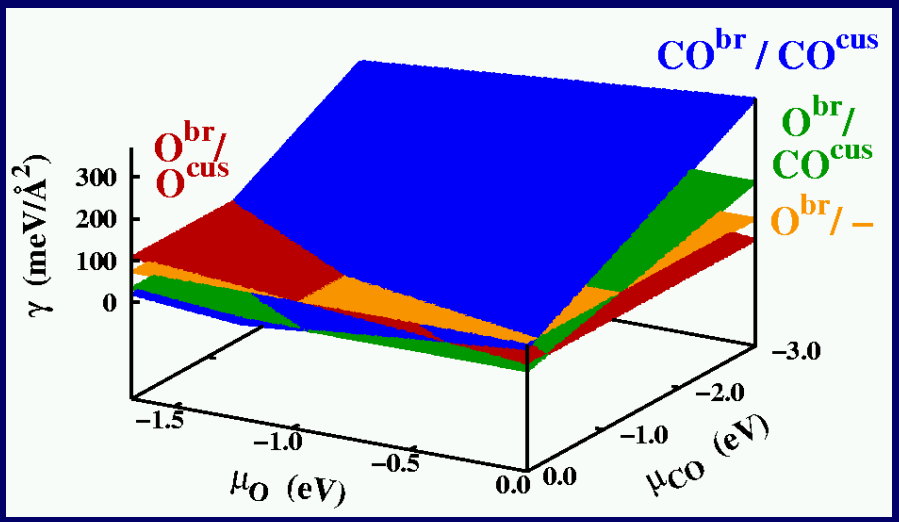


high pressure termination →



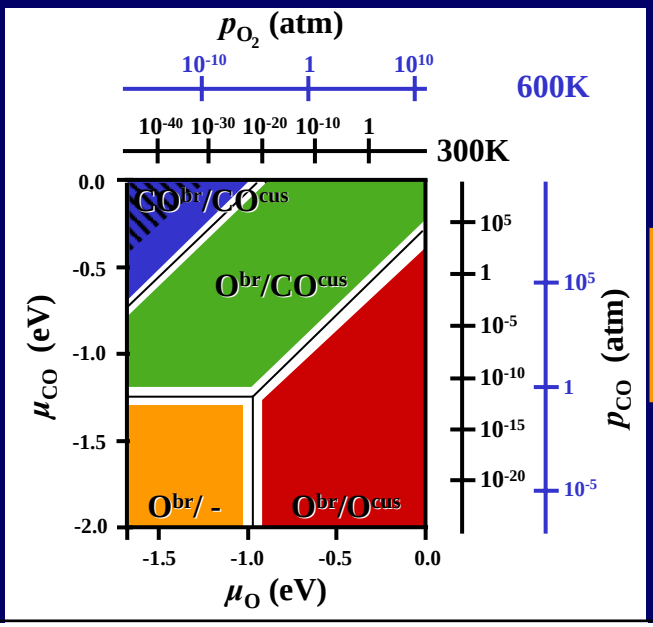
K. Reuter et al., PRB 65 (2001)

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

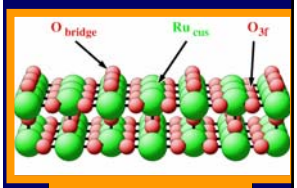


K. Reuter & M.S., PRL 90, 046103 (2003)

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



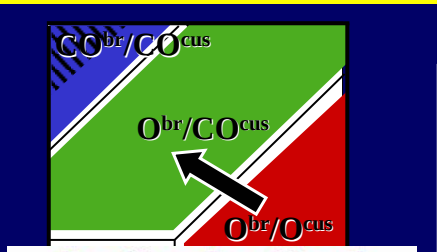
For a "constrained equilibrium"

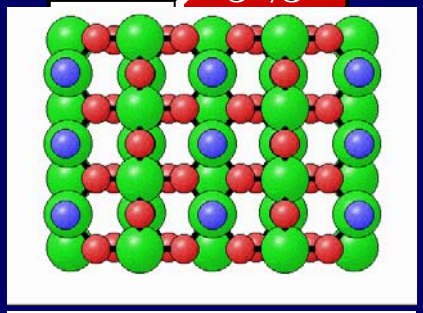


UHV surface termination

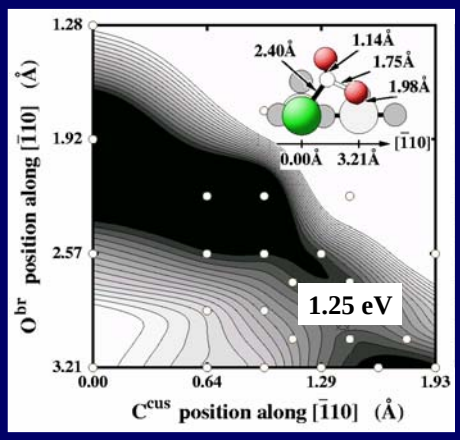
K. Reuter & M.S., PRL 90, 046103 (2003)

Possible reaction mechanisms: $CO^{cus} + O^{br} \rightarrow CO_2$



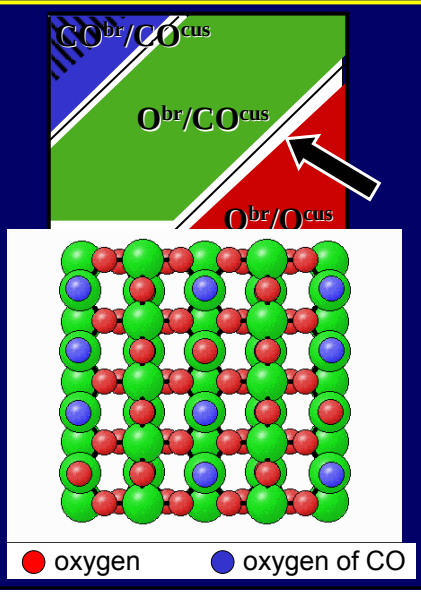


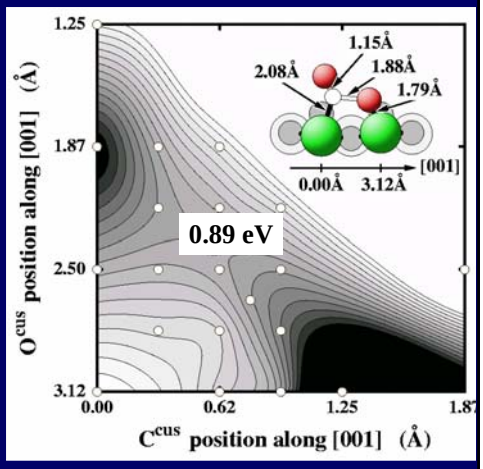
oxygen oxygen of CO



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

Possible reaction mechanisms:
$CO^{cus} + O^{cus} \rightarrow CO_2$





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

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

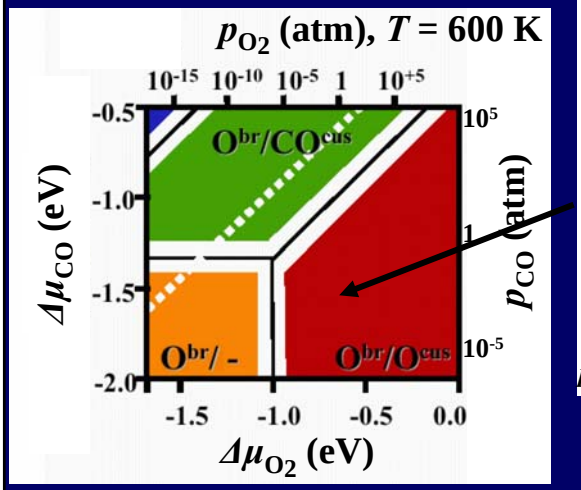
3) Statistical approach to describe
   - dissociation, adsorption, desorption
   - diffusion
   - reaction (CO_2 formation)
   - desorption of the product

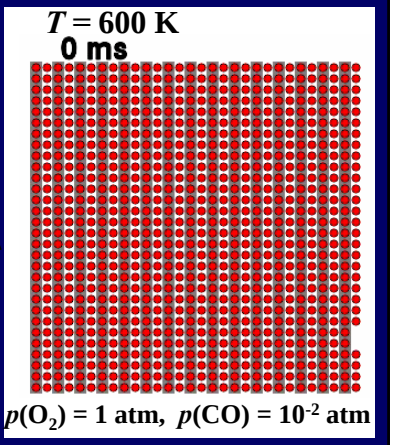
➡ **kinetic Monte Carlo method**

movies

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

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



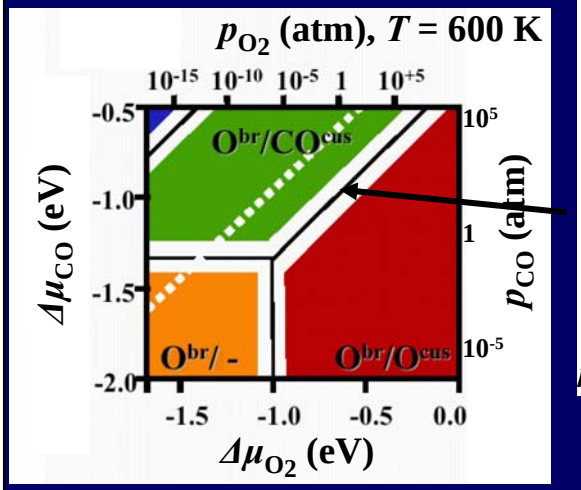


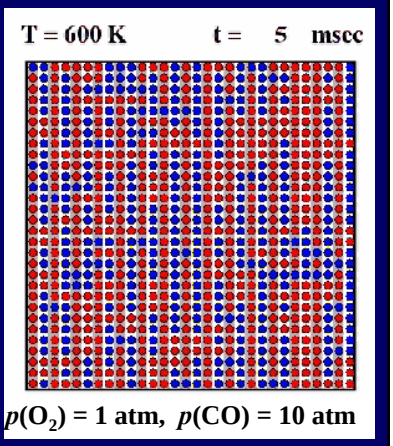
cus sites: white background
bridge sites: grey background

oxygen CO

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

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



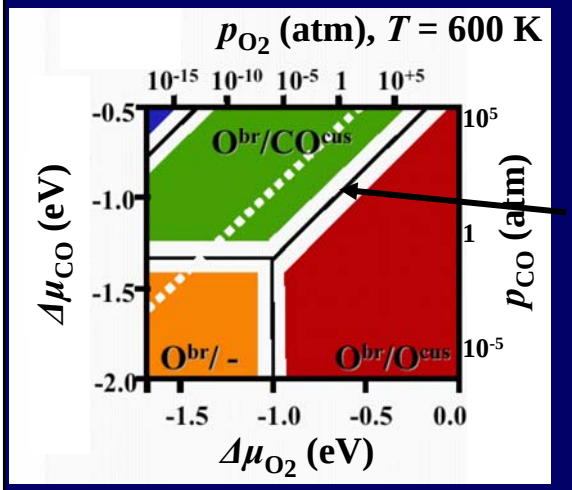


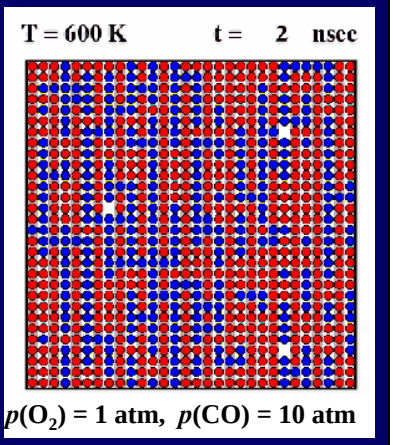
cus sites: white background
bridge sites: grey background

oxygen CO

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

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





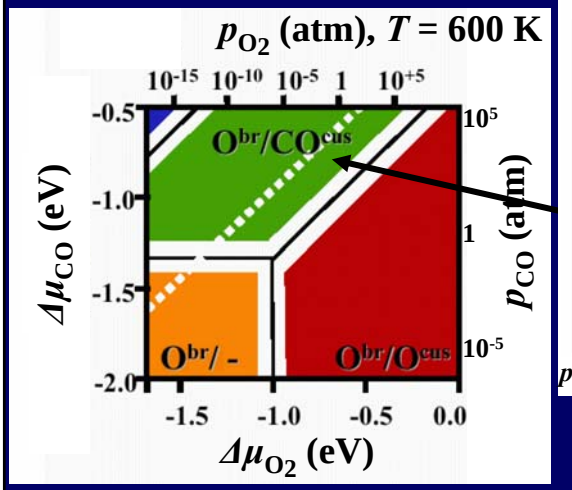
$p(O_2)$ = 1 atm, $p(CO)$ = 10 atm

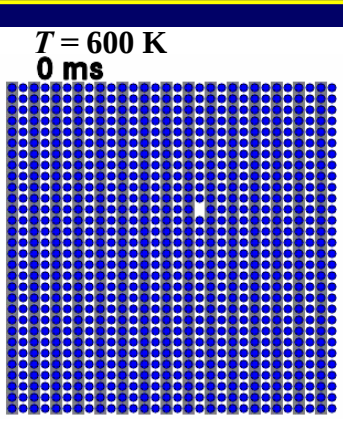
cus sites: white background
bridge sites: grey background

oxygen CO

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

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





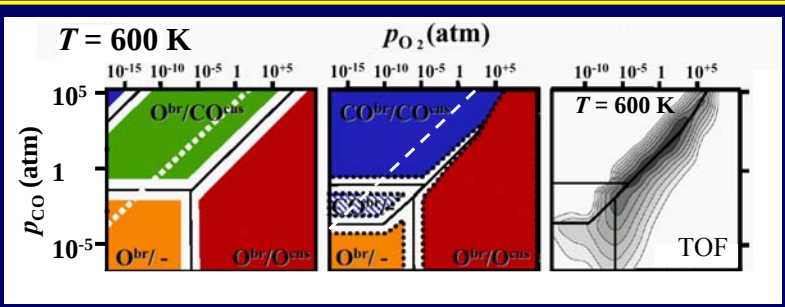
$p(O_2)$ = 1 atm, $p(CO)$ = 10^3 atm

cus sites: white background
bridge sites: grey background

oxygen CO

RuO_2 (110) high reactivity regions

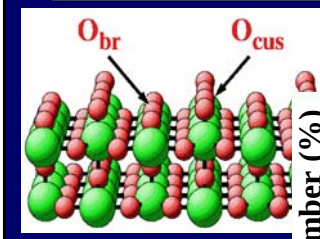
(bridging the pressure gap) *K. Reuter and M.S., to be published.*



- 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} (0.8eV), CO^{cus} + O^{br} (1.2 eV) . The rate is $r_{CO_2} = 10^{18}$ cm^{-2} s^{-1} .

Site occupation statistics at the steady state

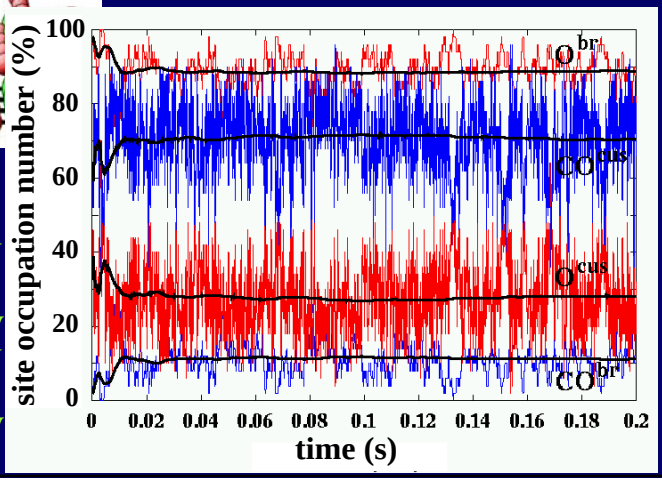
K. Reuter, D. Frenkel, and M.S., submitted.



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

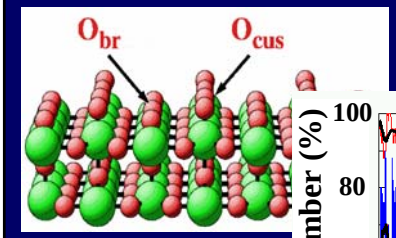
CO^{br} +O^{cus} : 0.8 eV
CO^{cus} +O^{br} : 1.2 eV

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



Site occupation statistics at the steady state

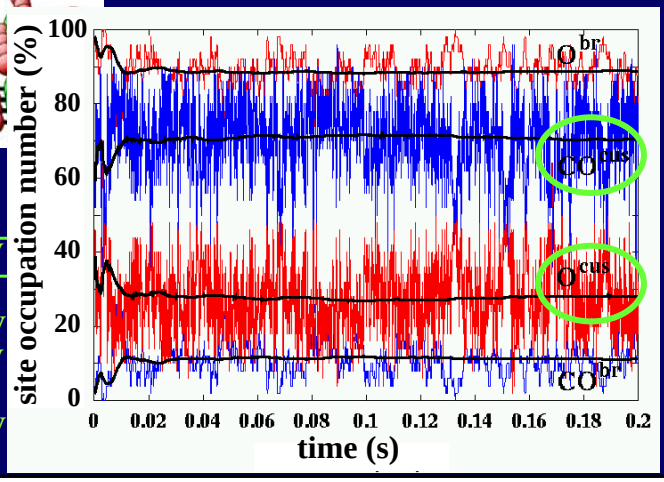
K. Reuter, D. Frenkel, and M.S., submitted.



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

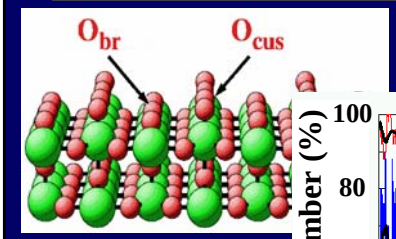
$CO^{br} + O^{cus}$: 0.8 eV
$CO^{cus} + O^{br}$: 1.2 eV

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



Site occupation statistics at the steady state

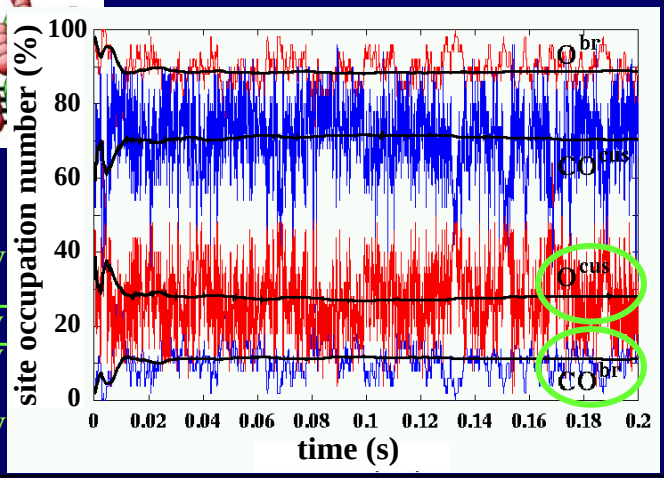
K. Reuter, D. Frenkel, and M.S., submitted.



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

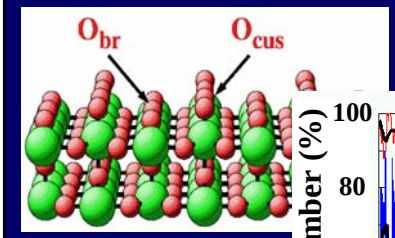
$CO^{cus} + O^{cus}$: 0.8 eV
$CO^{cus} + O^{br}$: 1.2 eV

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



Site occupation statistics at the steady state

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

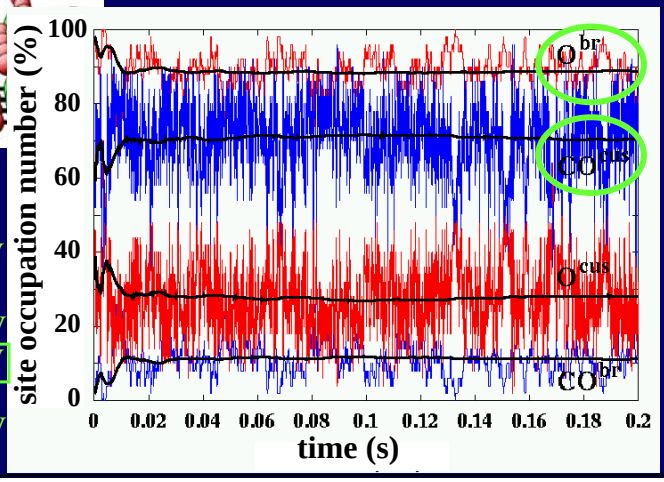


$CO^{cus} + O^{cus}$: 0.9 eV

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

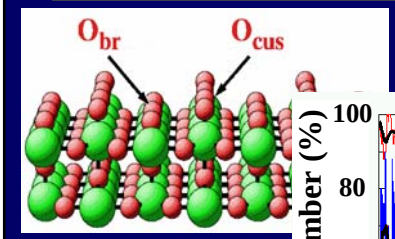
$CO^{cus} + O^{br}$: 1.2 eV

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



Site occupation statistics at the steady state

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

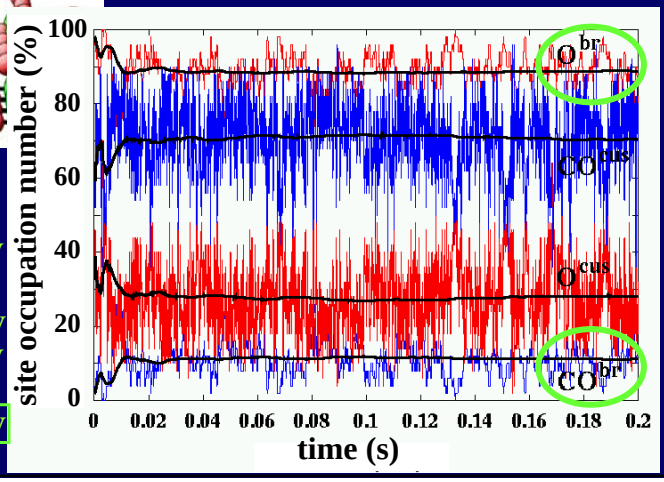


$CO^{cus} + O^{cus}$: 0.9 eV

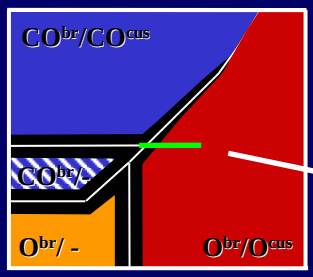
$CO^{br} + O^{cus}$: 0.8 eV

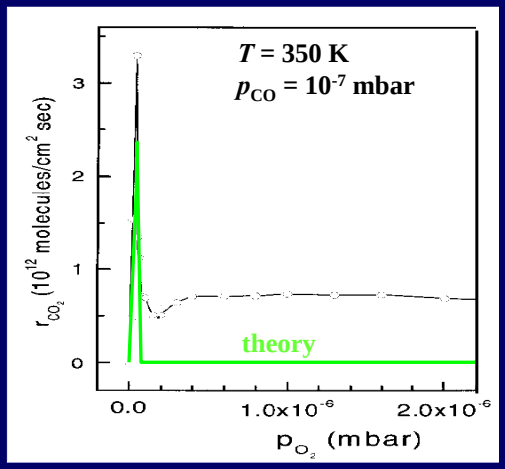
$CO^{cus} + O^{br}$: 1.2 eV

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



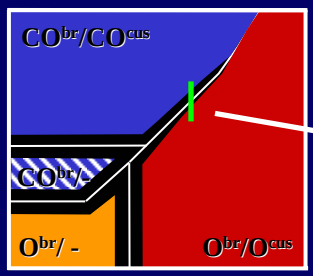
Comparison with experimental results

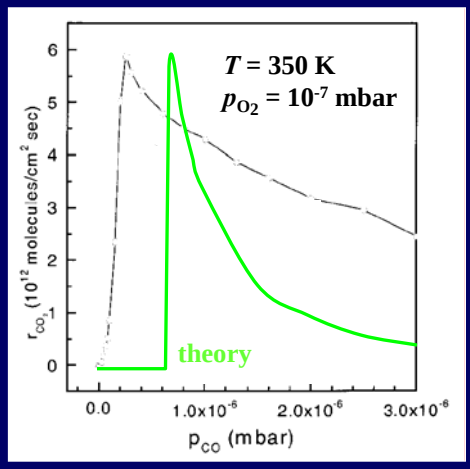




J. Wang, C.Y. Fan, K. Jacobi, and G. Ertl, J. Phys. Chem. B 106, 3422 (2002)

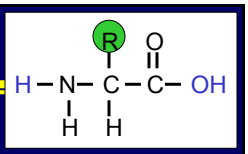
Comparison with experimental results



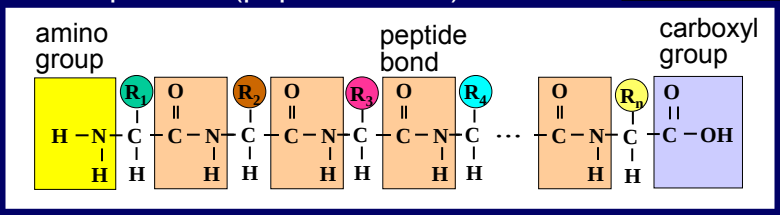


J. Wang, C.Y. Fan, K. Jacobi, and G. Ertl, J. Phys. Chem. B 106, 3422 (2002)

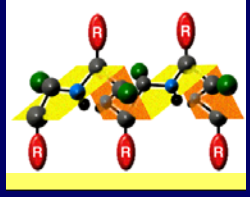
Stability of the α-helix



structure of proteins (peptide chains):

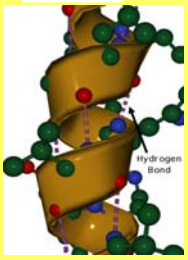


β sheet



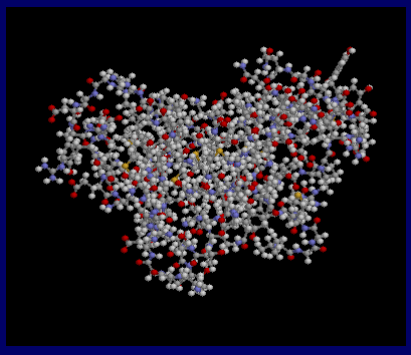
secondary structure

α helix



Folding of the peptide chain

peptide chain in the bovine prion protein

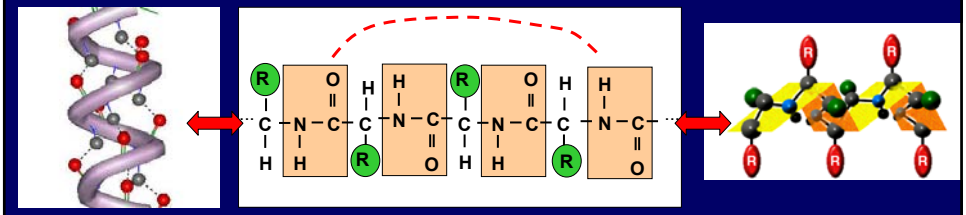


atomic structure

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 : $\Delta H^N_{\text{bb}} \approx 6.5$ *kcal/mol* for all N

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

$= -9.5$ *kcal/mol* for $N = \infty$

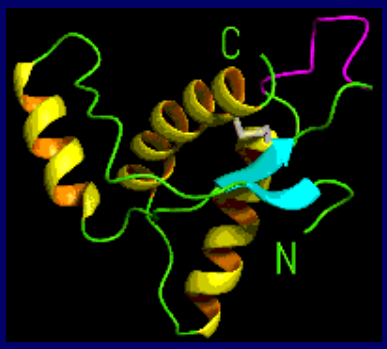
→ **hydrogen bond is strongly cooperative**

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**

↓

Statistical Mechanics

↘ ↙

Real World

Thermal Equilibrium Structures

The people behind the work

Cathy Stampfl

Joel Ireta

Karsten Reuter

et al. …

Peter Kratzer

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