

First-principles statistical mechanics of surfaces

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Thermodynamics

Why thermodynamics for materials?

A material is a collection of a large number of particles -- statistics starts to play a significant role at finite T

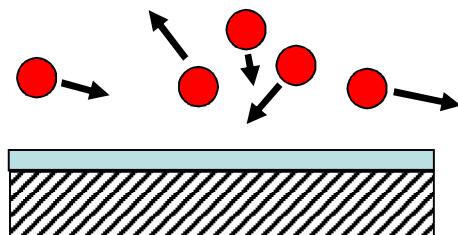
Thermodynamics determines defect concentrations and phase transformations, and influences magnetic properties, surface reactions, and crystal growth (the latter two are controlled by *kinetics*)

There is always a particle exchange between the material and its environment at finite T

Thermodynamics

□ Example

Consider a metal surface in an oxygen atmosphere



$$v = \frac{p}{\sqrt{2\pi mkT}}$$

For $T = 300 \text{ K}$, $p = 1 \text{ atm} \rightarrow v \sim 10^8 \text{ site}^{-1} \text{ s}^{-1}$



Requires $p \leq 10^{-12} \text{ atm}$ to keep a “clean” surface clean; surface can also lose atoms

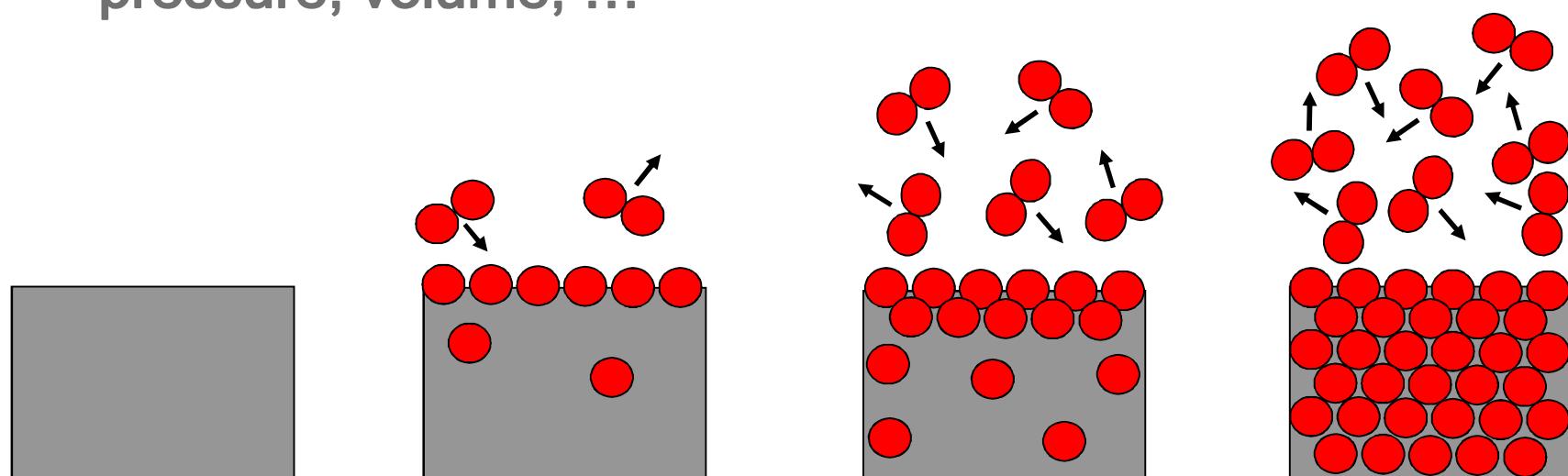
Adsorption will take place until the equilibrium is reached

Thermodynamics

□ Example

Consider a metal surface in an oxygen atmosphere

The point of equilibrium depends on temperature,
pressure, volume, ...



Thermodynamics

□ Thermodynamic potentials

Internal energy $U(S, V, \{N\})$

Enthalpy $H(S, p, \{N\}) = U + pV$

Helmholtz free energy $F(T, V, \{N\}) = U - TS$

Gibbs free energy $G(T, p, \{N\}) = U - TS + pV$

Energy balance equation

$$dU = TdS - pdV + \sum_i \mu_i dN_i$$

with chemical potentials

$$\mu_i = \left(\frac{\partial U}{\partial N_i} \right)_{S,V} = \left(\frac{\partial H}{\partial N_i} \right)_{S,p} = \left(\frac{\partial F}{\partial N_i} \right)_{T,V} = \left(\frac{\partial G}{\partial N_i} \right)_{T,p}$$

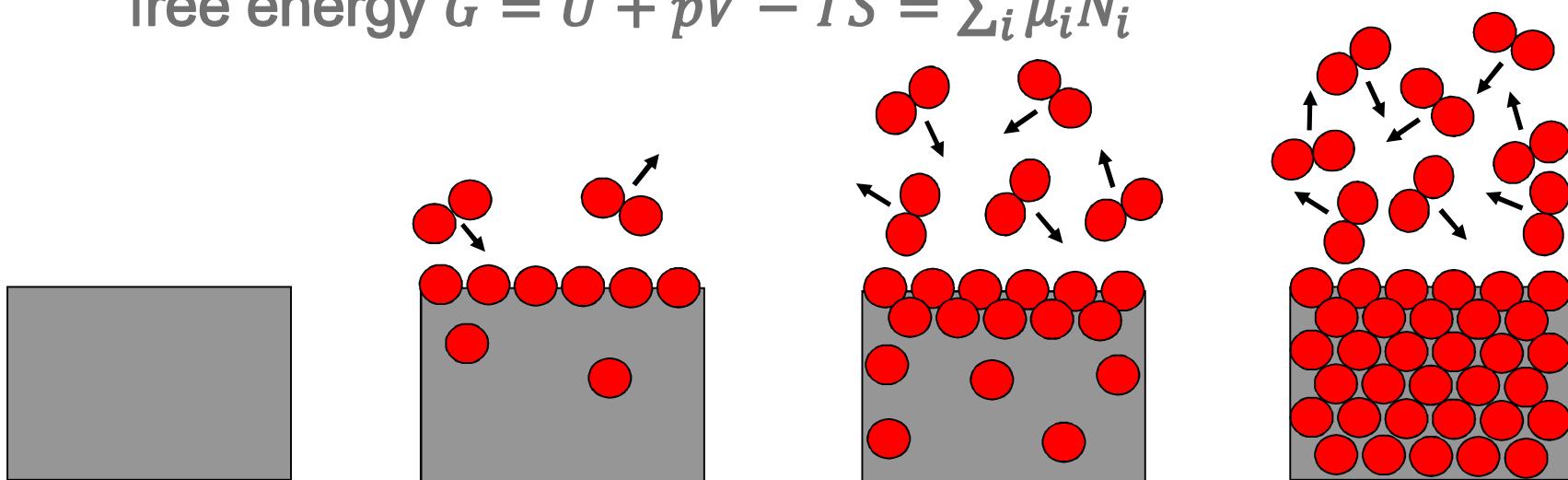
Thermodynamics

Reaching the equilibrium

At constant T a system minimizes its free energy ($-TS$), not the internal energy U

If also volume V is constant, the energy minimized is the Helmholtz free energy $F = U - TS$

If (T, p) are constant, the energy minimized is the Gibbs free energy $G = U + pV - TS = \sum_i \mu_i N_i$



Thermodynamics

Statistical thermodynamics



$$S = k \log W$$

W - number of *microstates* for a given *macrostate*

This is “only” a postulate - but it works!

Why it should work: (i) in equilibrium $W \rightarrow \text{max}$, so that $S \rightarrow \text{max}$; (ii) S is additive, but W is multiplicative

Thermodynamics

Statistical thermodynamics

Let us consider a system that can be in one of states i with energy E_i

At a given T , the probability of the system to be in state i is $P_i = \frac{e^{-E_i/kT}}{Z}$, $Z = \sum_i e^{-E_i/kT}$, $\sum_i P_i = 1$

Ergodic hypothesis: average over time is equal to the average over ensemble - holds if all states are equiprobable (for most realistic systems)

What are the average values of entropy and thermodynamic potentials?

Thermodynamics

□ Statistical thermodynamics

Consider the ensemble of N replicas of the system - let us count microstates of this ensemble

A microstate describes which replicas are in which state, while a macrostate describes how many replicas are in each state; thus: $W = \frac{N!}{N_1!(N-N_1)!} \frac{(N-N_1)!}{N_2!(N-N_1-N_2)!} \dots = \frac{N!}{N_1!N_2! \dots}$
where N_1, N_2, \dots are the numbers of the replicas in state 1, 2, ...

$$N_i = NP_i = N \frac{e^{-E_i/kT}}{Z}, \tilde{S} = k \ln W = k \ln(N!) - k \sum_i \ln(N_i!)$$

Z - canonical partition function

Use Stirling's formula: $\ln(N!) \approx N \ln N - N$

Thermodynamics

□ Statistical thermodynamics

$$\tilde{S} = k \ln W = N k \ln Z + \frac{N}{T Z} \sum_i E_i e^{-E_i/kT}$$

Internal energy, by definition: $\tilde{U} = \frac{N}{Z} \sum_i E_i e^{-E_i/kT} = \frac{NkT^2}{Z} \frac{\partial Z}{\partial T}$

$$U = \frac{\tilde{U}}{N} = \frac{kT^2}{Z} \frac{\partial Z}{\partial T} = kT^2 \frac{\partial \ln Z}{\partial T}$$

$$S = \frac{\tilde{S}}{N} = \frac{k \ln W}{N} = k \ln Z + \frac{U}{T} = k \ln Z + kT \frac{\partial \ln Z}{\partial T}$$

$$F = U - TS = -kT \ln Z$$

$$G = F + pV = -kT \ln Z + pV$$

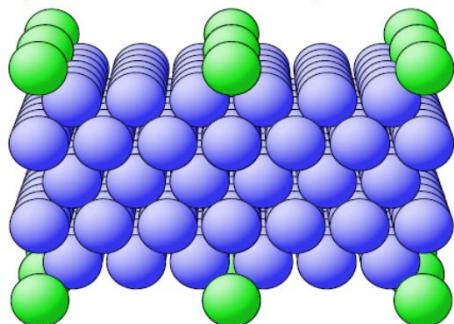
$$\mu(T, p) = \left(\frac{\partial G}{\partial N} \right)_{T,p} = \frac{\partial}{\partial N} (-kT \ln Z + pV)_{T,p}$$

The supercell approach

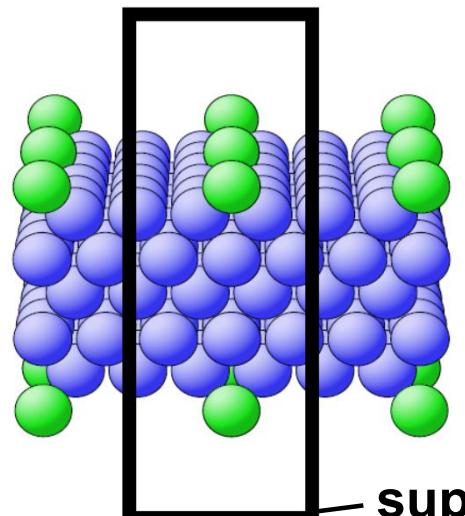
Can we benefit from periodic modeling of non-periodic systems?

Yes, for interfaces (surfaces) and wires (also with adsorbates), and defects (especially for concentration or coverage dependences)

Supercell approach to surfaces (slab model)



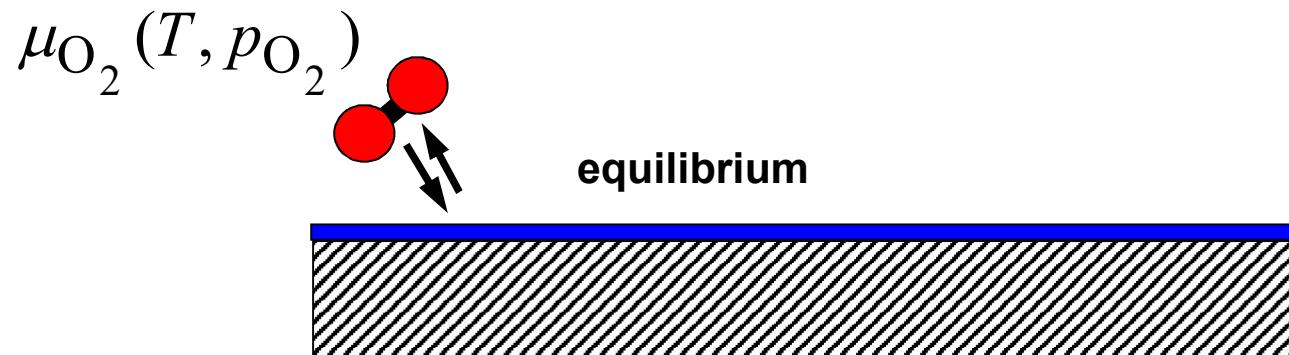
- Approach accounts for the lateral periodicity
- Sufficiently broad vacuum region to decouple the slabs
- Sufficient slab thickness to mimic semi-infinite crystal
- Semiconductors: saturate dangling bonds on the back surface
- Non-equivalent surfaces: use dipole correction
- Alternative: cluster models (for defects and adsorbates)



Thermodynamics

□ Statistical thermodynamics

Practical example: surface free energy



Change in Gibbs free energy upon addition of O to the surface: $\Delta G = G_{surf}(N_O + 1) - \left(G_{surf}(N_O) + \frac{1}{2} \mu_{O_2} \right)$

$$\text{since } \mu_O = \frac{1}{2} \mu_{O_2}$$

Goal - find surface composition and structure that minimizes G at given T, p

Thermodynamics

□ Statistical thermodynamics

Practical example: surface free energy

$$\Delta\gamma(N_O, T, p) = \frac{1}{A} [G_{surf}(N_O, T, p) - G_{surf}(N_O^{ref}, T, p) - \mu_O(N_O - N_O^{ref})] \rightarrow \min_{N_O}$$

where A is the surface area, N_O^{ref} is the number of O atoms in the reference system

$$G_{surf}(N_O) - G_{surf}(N_O^{ref}) = \Delta E_{surf} + \Delta U_{vib} - T\Delta S_{vib} - T\Delta S_{conf} + p\Delta V$$

$\mu_O(T, p)$ - ?

Thermodynamics

□ Statistical thermodynamics

Let us consider a gas of N non-interacting diatomic (for simplicity) molecules

Each molecule has the following degrees of freedom:
nuclear, electronic, *translational*, rotational, vibrational

$$Z = \frac{(z_{transl})^N}{N!} (z_{rot})^N (z_{vib})^N (z_{el})^N (z_{nucl})^N$$

 translational states are invariant with respect to any permutations of molecules (indistinguishable molecules)

z_x - partition function for the degree of freedom x for a single molecule

Thermodynamics

□ Statistical thermodynamics

$$\mu(T, p) = \frac{\partial}{\partial N} (-NkT \ln(z_{transl}) + kT \ln N! - NkT \ln(z_{rot}) - NkT \ln(z_{vib}) - NkT \ln(z_{el}) - NkT \ln(z_{nucl}) + pV)_{T,p}$$

Remember ideal gas law $pV = NkT$ and Stirling's formula

$$\mu(T, p) = -kT \ln\left(\frac{z_{transl}}{N}\right) - kT \ln(z_{rot}) - kT \ln(z_{vib}) - kT \ln(z_{el}) - kT \ln(z_{nucl}) + kT$$

$$\frac{z_{transl}}{N} = \frac{V}{N} \int e^{-\frac{\hbar \mathbf{k}^2}{2mkT}} d^3 \mathbf{k} = \frac{V}{N} \left(\frac{2\pi m k T}{\hbar^2} \right)^{\frac{3}{2}} = \frac{kT}{p} \left(\frac{2\pi m k T}{\hbar^2} \right)^{\frac{3}{2}}$$

required input - molecule's mass m

$$z_{el} = \sum_i (2s_i + 1) e^{-\frac{E_i}{kT}} \approx (2s_0 + 1) e^{-\frac{E_0}{kT}} \rightarrow \mu_{el} \approx E_0 - kT \ln(2s_0 + 1)$$

required input - E_0 , s_0

Thermodynamics

□ Statistical thermodynamics

$$z_{rot} = \frac{1}{\sigma} \sum_J (2J + 1) e^{-\frac{B_0 J(J+1)}{kT}} \approx \frac{1}{\sigma} \int_0^{\infty} (2J + 1) e^{-\frac{B_0 J(J+1)}{kT}} dJ = \frac{T}{\sigma \theta_r}$$

where $\sigma = 2$ for homonuclear molecules
(indistinguishable with respect to permutation of the two identical nuclei), $\sigma = 1$ for heteronuclear molecules,

$$\theta_r = \frac{\hbar^2}{2kI}, I = \frac{m_A m_B}{m_A + m_B} d^2, d \text{ is the bond length}$$

$$\mu_{rot} \approx -kT \ln \left(\frac{2kTI}{\sigma \hbar^2} \right), \text{ required input - rotational constant}$$

(calculated or from microwave spectroscopy)

Thermodynamics

□ Statistical thermodynamics

$$z_{vib} = \prod_{i=1}^M \sum_{n=0}^{\infty} e^{-(n+\frac{1}{2})\frac{\hbar\omega_i}{kT}} = \prod_{i=1}^M e^{-\frac{\hbar\omega_i}{2kT}} \sum_{n=1}^{\infty} e^{-\frac{n\hbar\omega_i}{kT}} =$$

$$= \prod_{i=1}^M \frac{e^{-\frac{\hbar\omega_i}{2kT}}}{1 - e^{-\frac{\hbar\omega_i}{kT}}} \quad (\text{used the fact that sum over } n \text{ is a geometric series})$$

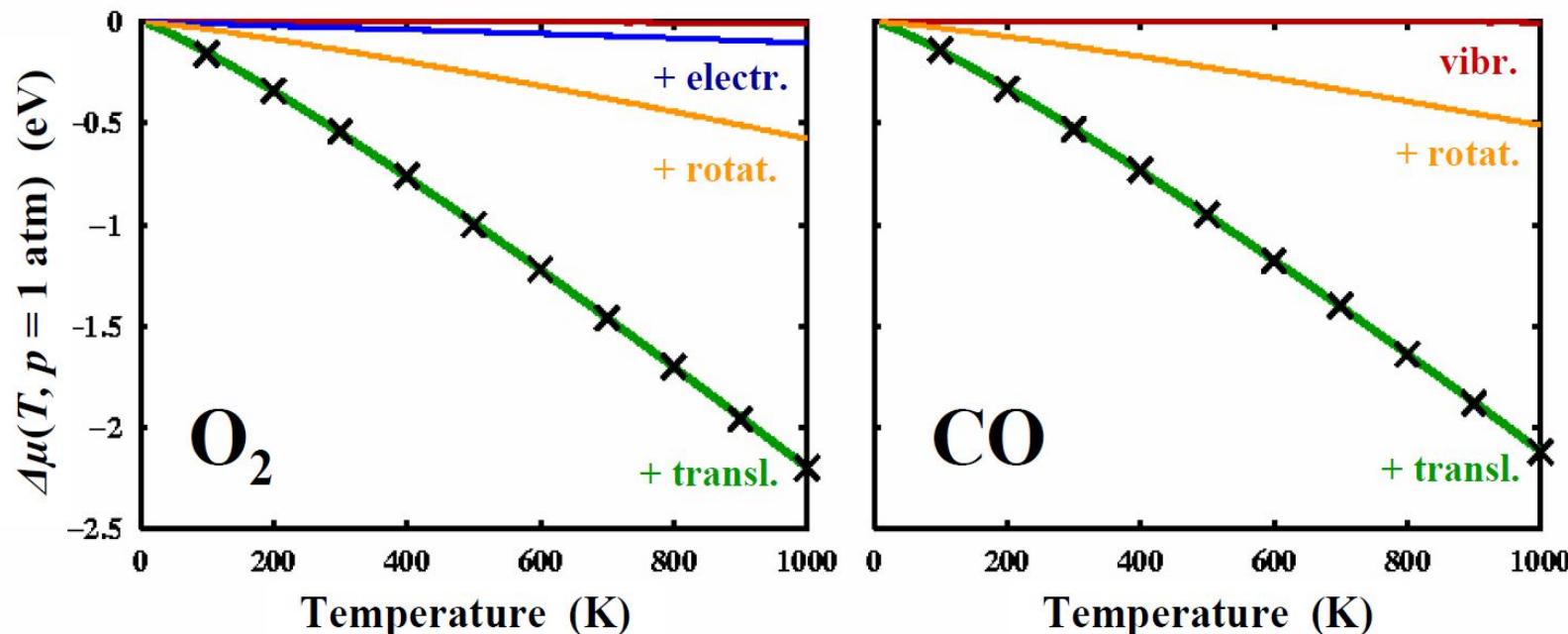
For a diatomic molecule $\mu_{vib} = \frac{\hbar\omega}{2} + kT \ln(1 - e^{-\hbar\omega/kT})$
required input - vibrational frequency ω

In most practical cases, we can neglect the interaction between nuclear spins, so that $z_{nucl} \approx 1$ (not correct at very low temperatures)

Thermodynamics

Ab initio atomistic thermodynamics

It is convenient to define a reference for $\mu(T, p)$: $\mu(T, p) = E_0 + \Delta\mu(T, p)$

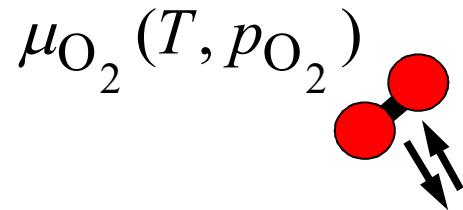


Alternatively: $\Delta\mu(T, p) = \Delta\mu(T, p^0) + k_B T \ln(p / p^0)$

and $\Delta\mu(T, p^0 = 1 \text{ atm})$ from thermochemical tables (e.g., JANAF)

Thermodynamics

□ *Ab initio* atomistic thermodynamics



$$\Delta\gamma(N_O, T, p) = \frac{1}{A} [\Delta E_{surf} + \Delta U_{vib} - T\Delta S_{vib} - T\cancel{\Delta S}_{conf} + p\cancel{\Delta V} - \mu_O \Delta N_O]$$

electronic structure calculations

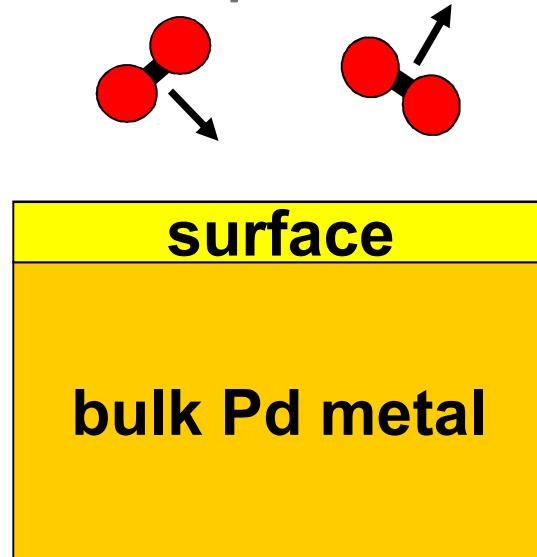
$$\Delta F_{vib}(T, V) = V \int_0^{\infty} f(T, \omega) (\sigma(\omega) - \sigma_{ref}(\omega)) d\omega, \quad \sigma(\omega) -$$

phonon density of states, $f(T, \omega) = \frac{\hbar\omega}{2} + kT \ln(1 - e^{-\hbar\omega/kT})$

Thermodynamics

Ab initio atomistic thermodynamics

Example: Metal surface in contact with O₂ gas



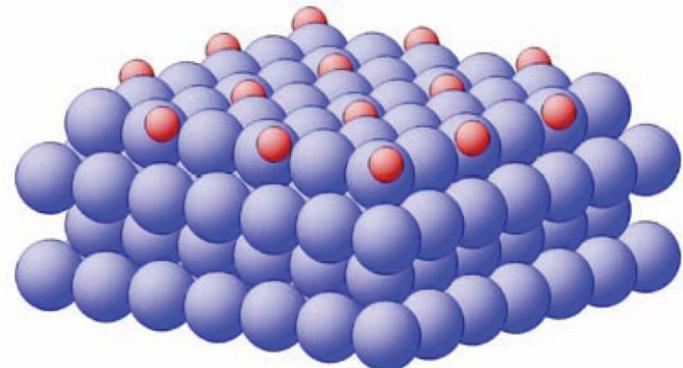
Reservoir: $\mu_O(T, p_{O_2})$ from ideal gas, $N_O^{ref} = 0$ (bare metal surface is the reference system), $\frac{1}{2}E_{O_2}$ is the reference for the chemical potential of O: $\mu_O = \Delta\mu_O + \frac{1}{2}E_{O_2}$

Neglect for now ΔF_{vib} and $T\Delta S_{conf}$

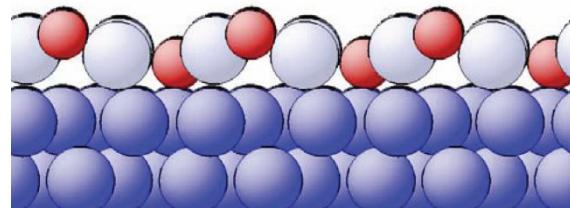
$$\Delta\gamma(T, p_{O_2}) = \frac{1}{A} \left[E_{surf}(N_O) - E_{surf}(0) - N_O \frac{1}{2}E_{O_2} \right] - \frac{1}{A} N_O \Delta\mu_O(T, p_{O_2})$$

Example: Pd(100)

$$\Delta\gamma(T, p_{O_2}) = \frac{1}{A} \Delta E_{surf}(N_O) - \frac{1}{A} N_O \Delta\mu_O(T, p_{O_2})$$

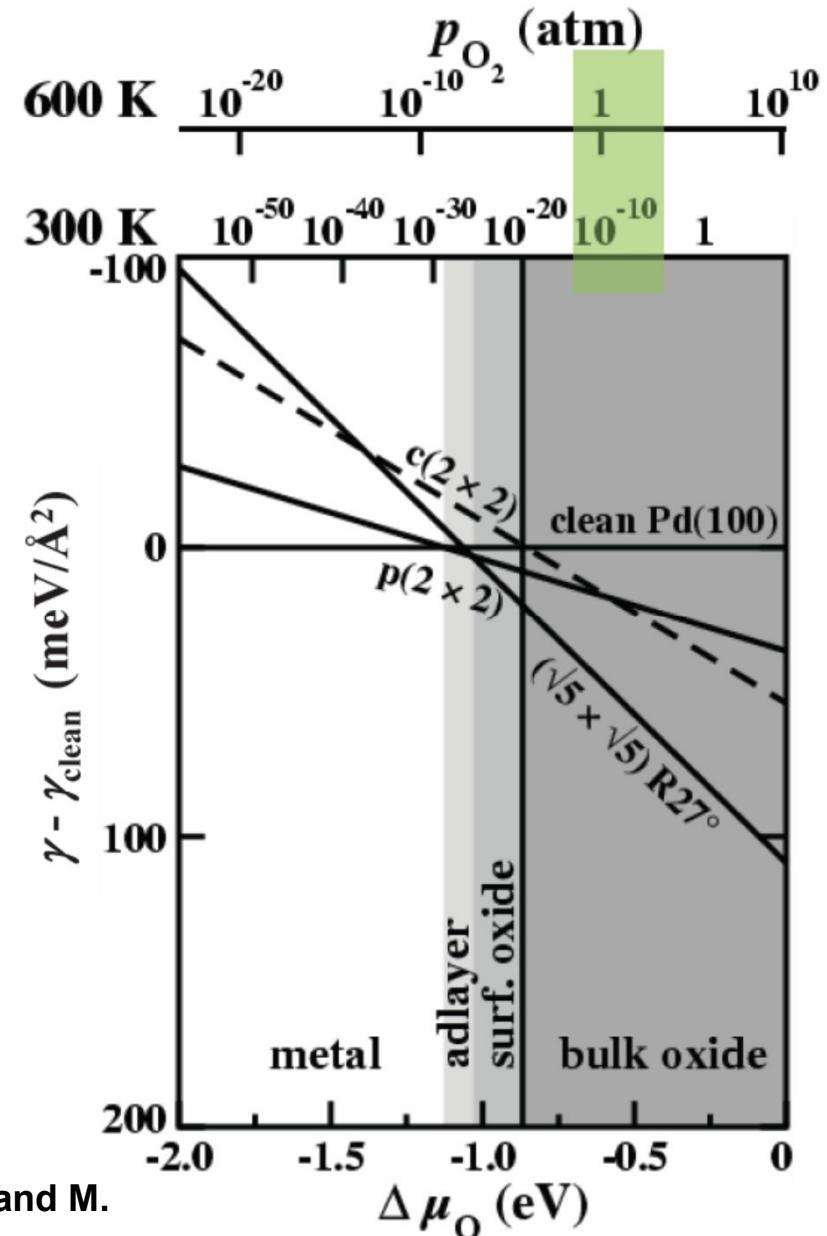


p(2x2) O/Pd(100)

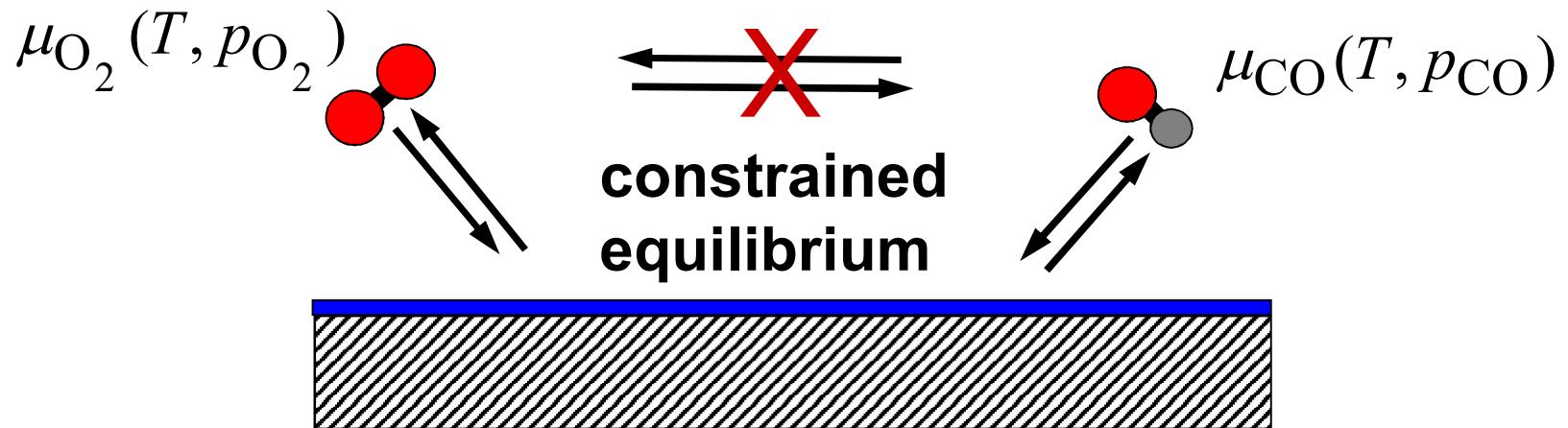


(sqrt(5)xsqrt(5))R27 degrees PdO(101)/Pd(100)

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



First-principles atomistic thermodynamics: constrained equilibria

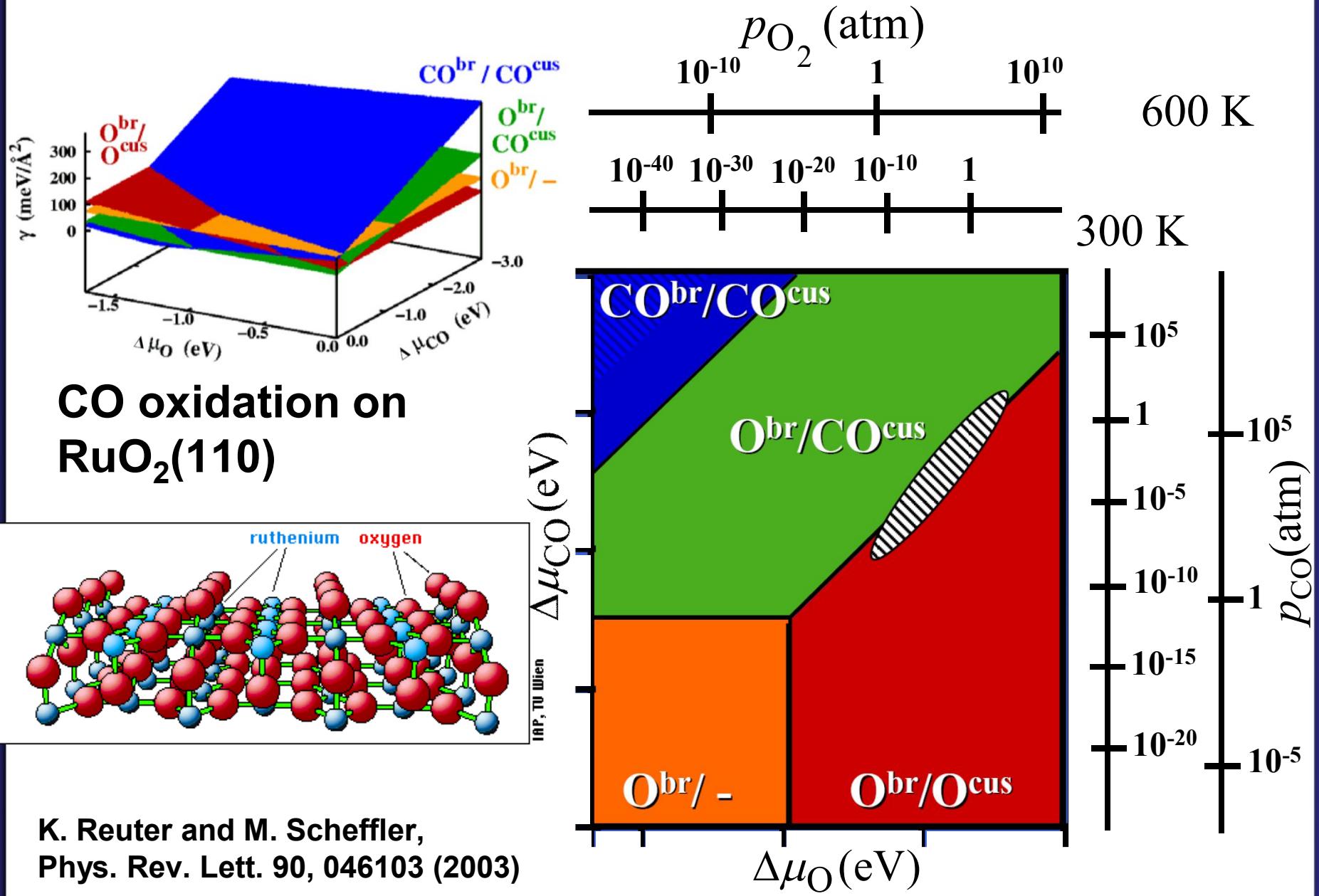


$$\Delta\gamma(T, p_{O_2}) = \frac{1}{A} \left[E_{surf}(N_O, N_{CO}) - E_{surf}^{ref} - N_O \frac{1}{2} E_{O_2} - N_{CO} E_{CO} \right]$$
$$- \frac{1}{A} N_O \Delta\mu_O(T, p_{O_2}) - \frac{1}{A} N_{CO} \Delta\mu_{CO}(T, p_{CO})$$

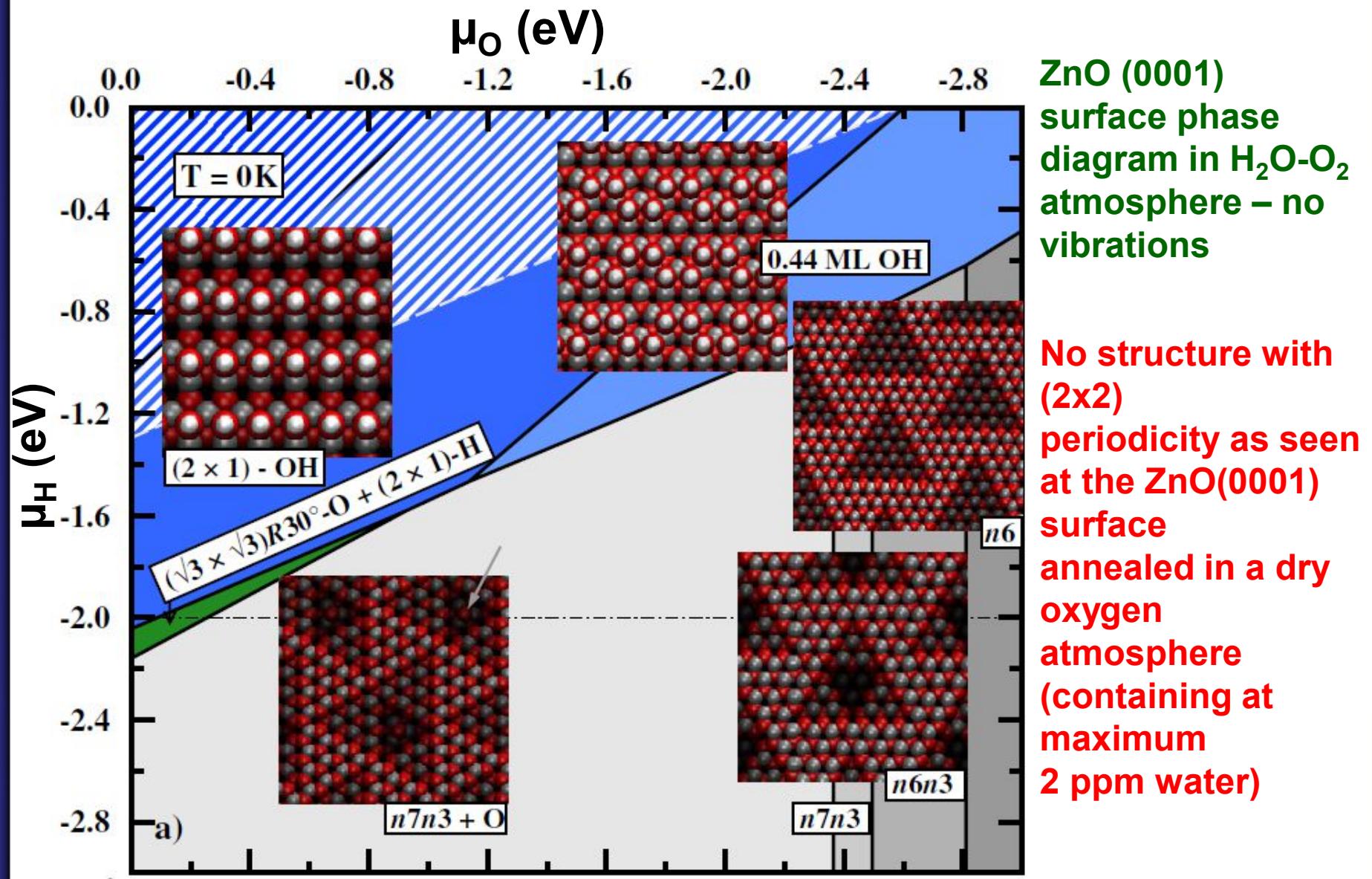
C.M. Weinert and M. Scheffler, Mater. Sci.
Forum 10-12, 25 (1986); E. Kaxiras *et al.*,
Phys. Rev. B 35, 9625 (1987);

K. Reuter and M. Scheffler,
Phys. Rev. B 65, 035406 (2001);
Phys. Rev. B 68, 045407 (2003)

Surface phase diagrams

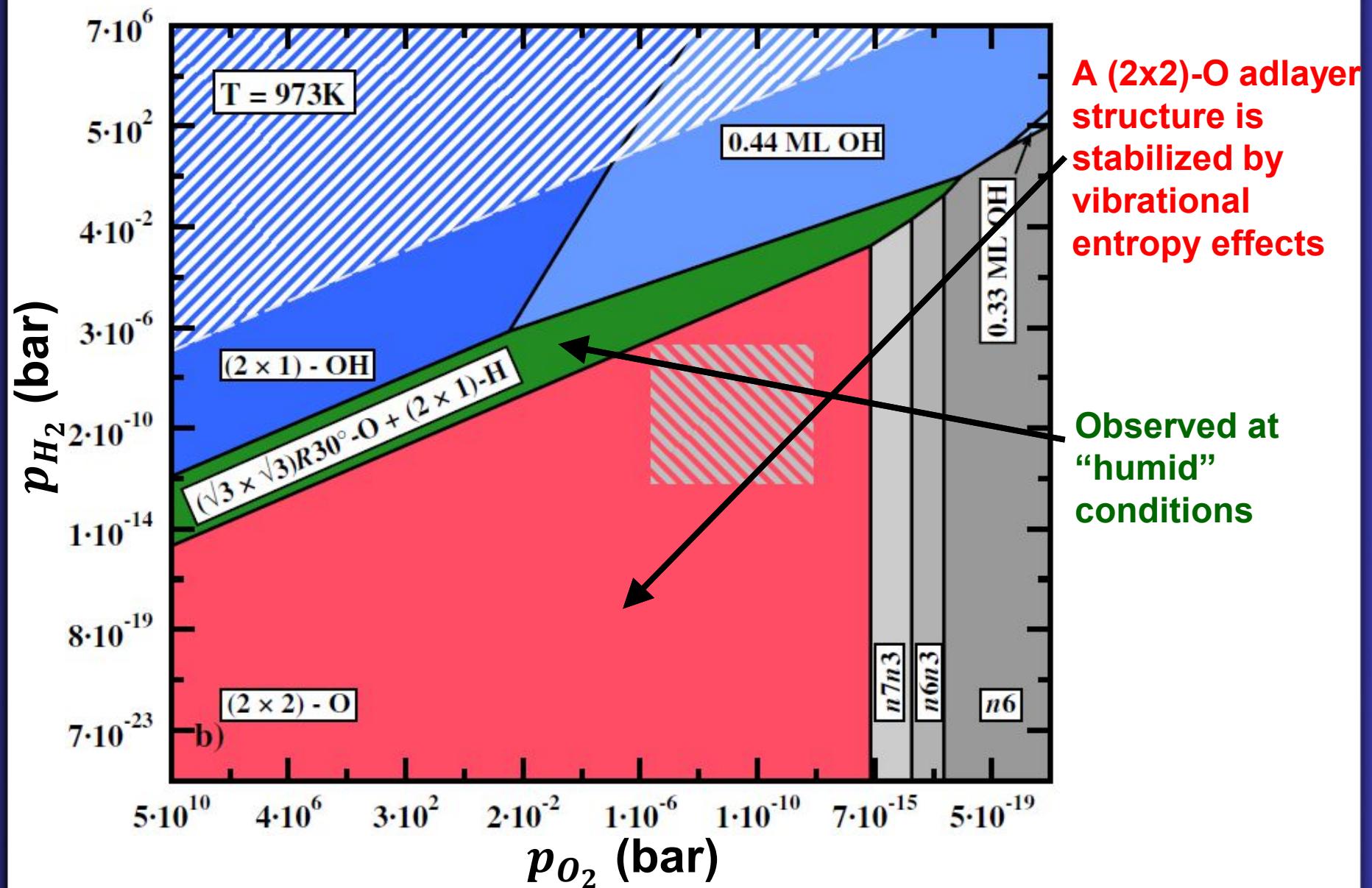


When vibrations do matter



M. Valtiner, M. Todorova, G. Grundmeier, and J. Neugebauer, PRL 103, 065502 (2009)

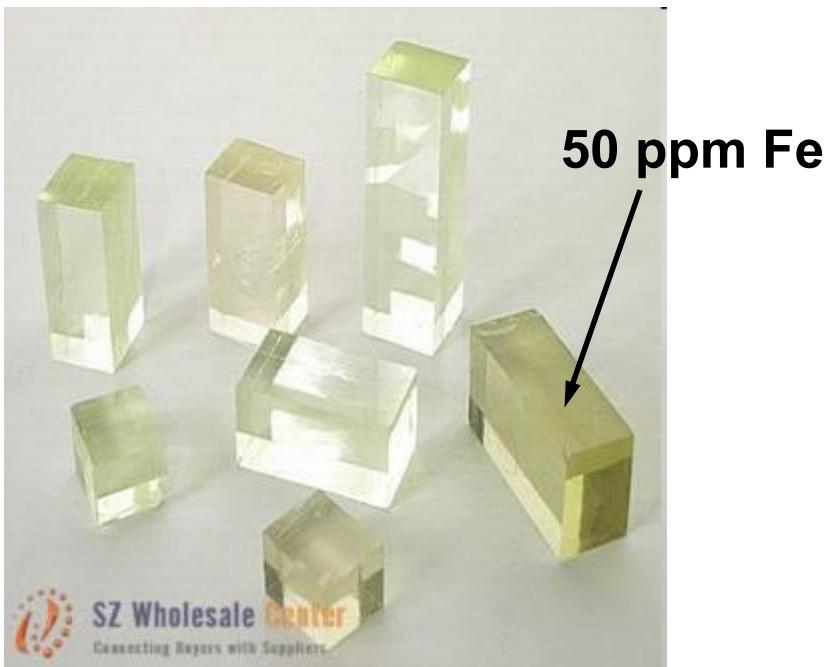
When vibrations do matter



M. Valtiner, M. Todorova, G. Grundmeier, and J. Neugebauer, PRL **103**, 065502 (2009)

Thermodynamics of Defects

- Very small concentrations of defects can significantly alter materials properties



Small concentration of Fe impurities are visible by naked eye in intrinsically transparent MgO

Si semiconductors contain 10^{-9} - 10^{-3} intentional impurities per atom

“My precious!”: Perfect defected gems



Cr: Al_2O_3



V: Al_2O_3



Fe: Al_2O_3



Fe: Al_2O_3

Impurities are responsible for the color of sapphire and many other precious stones

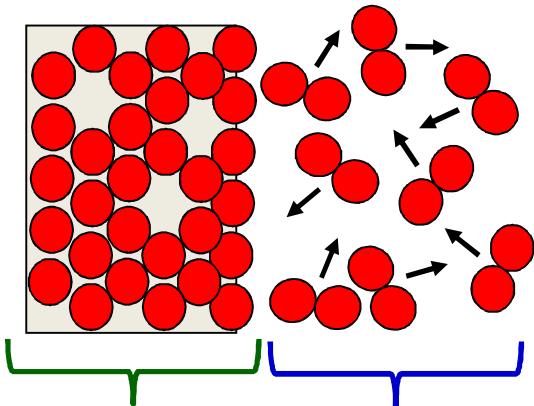
Typical concentrations: 100-10000 ppm



Fe,Ti: Al_2O_3

Entropy

$$G = U + pV - TS$$



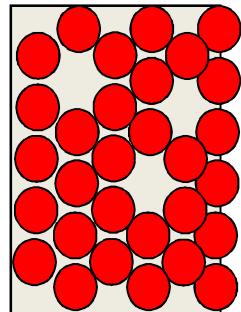
$$S = k \ln W$$

W – number of microstates

- 1) Solid: vibrational entropy (phonons)
- 2) Solid: electronic entropy
- 3) Gas: vibrational, rotational, translational, etc. (part of μ_i)
- 4) Solid: defect disorder

Configurational entropy

$$G = [U + pV - T(S - S_{\text{config}})] - TS_{\text{config}} = \tilde{G} - TS_{\text{config}}$$



N equivalent defect sites in the sold

n defects

If defects do not interact: $S_{\text{config}} = k \ln \frac{N!}{n!(N-n)!}$

Stirling's formula:

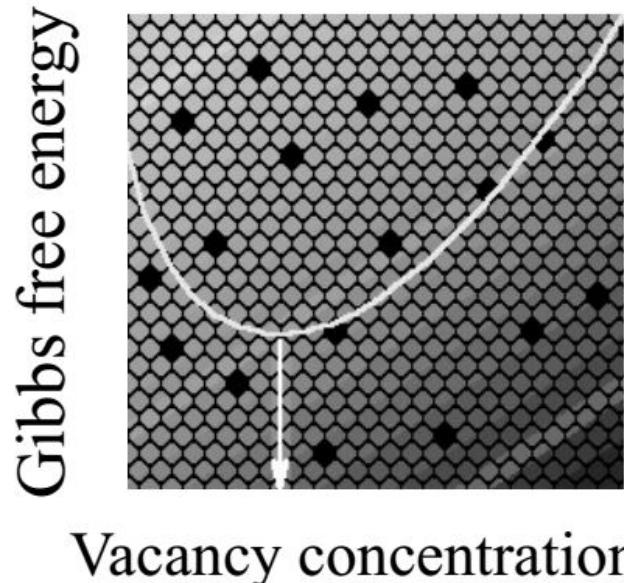
$$\ln(n!) = n(\ln n - 1 + \delta), \quad n \gg 1, \quad \delta \sim \frac{\ln(2\pi n)}{2n}$$

$$S_{\text{config}} \approx k[N \ln N - n \ln n - (N-n) \ln(N-n)]$$

Good approximation only on a macroscopic scale

Defect concentration

Minimize the free energy of the system with respect to the number of defects



$$G(n) = \tilde{G}_0 + n\Delta G_f - TS_{\text{config}}(n)$$

If defects do not interact:

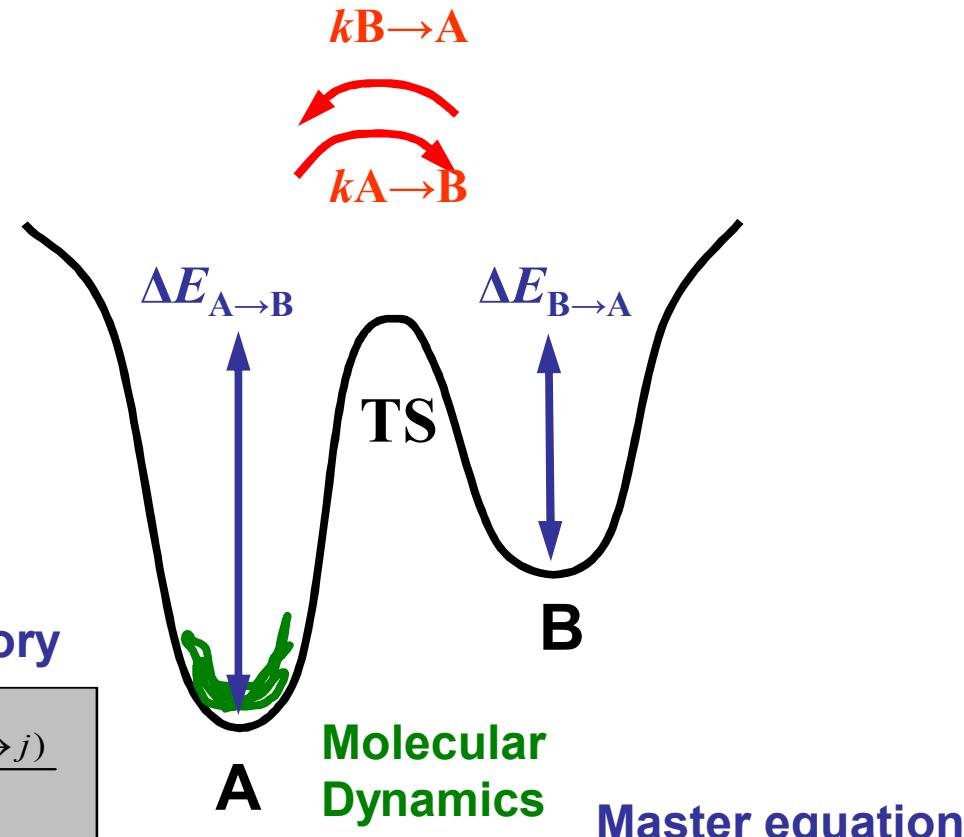
$$\frac{n}{N} = \frac{1}{\exp(\Delta G_f/kT) + 1}$$

$$\frac{n}{N} \ll 1 \Leftrightarrow \exp(\Delta G_f/kT) \gg 1$$

$$\frac{n}{N} \approx \exp(-\Delta G_f(T, p)/kT) - \text{textbook formula}$$

Monte Carlo sampling - applications

□ Reaction kinetics - kinetic MC (kMC)



Transition State Theory

$$k_{i \rightarrow j} = \left(\frac{k_B T}{h} \right) \frac{Z_{TS(i \rightarrow j)}}{Z_i}$$
$$= \Gamma_o \exp \left(\frac{-\Delta E_{i \rightarrow j}}{k_B T} \right)$$

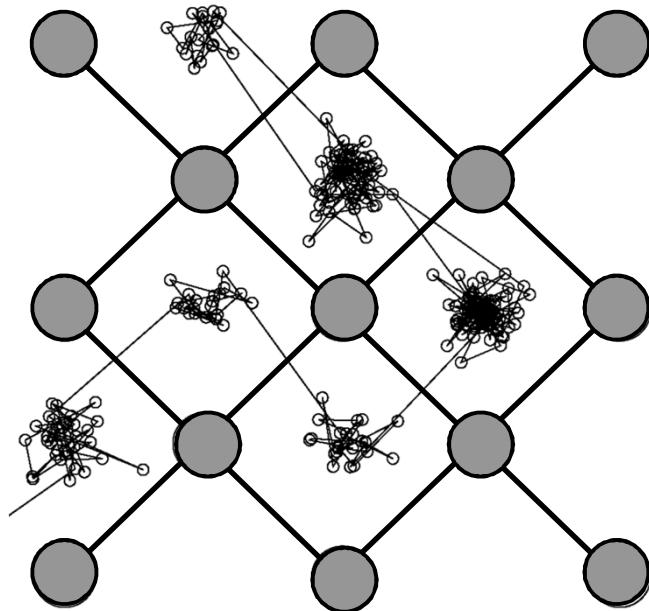
Molecular
Dynamics

Master equation

$$\frac{dP_i(t)}{dt} = - \sum_j k_{i \rightarrow j} P_i(t) + \sum_j k_{j \rightarrow i} P_j(t)$$

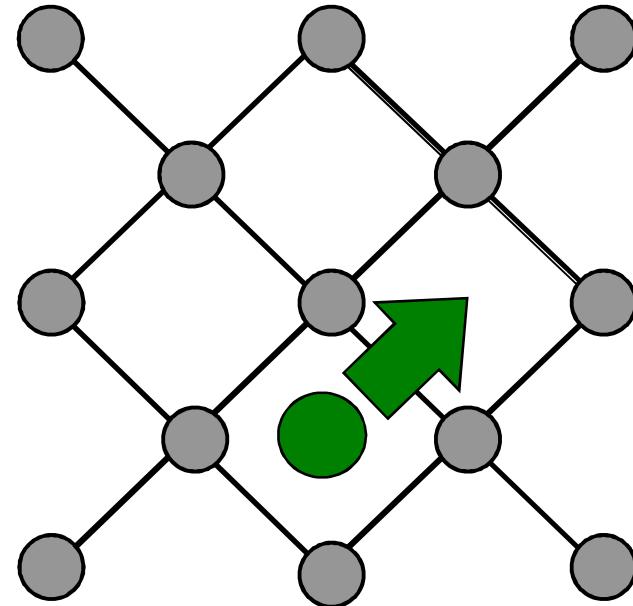
Monte Carlo sampling - applications

Reaction kinetics - kinetic MC (kMC)



Molecular Dynamics:
the whole trajectory

ab initio MD:
up to 50 ps



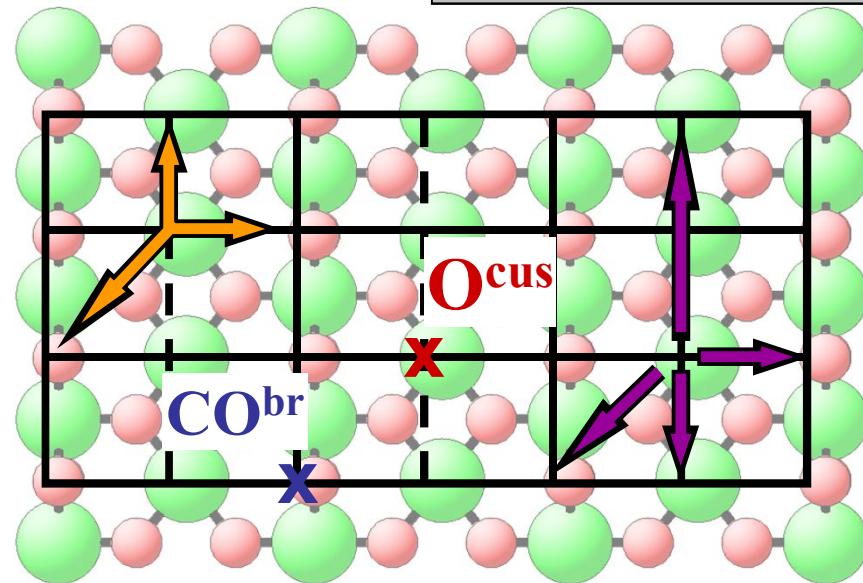
Kinetic Monte Carlo:
coarse-grained hops

ab initio kMC:
up to minutes

Monte Carlo sampling - applications

□ Crucial ingredients of kMC

$$\frac{dP_i(t)}{dt} = -\sum_j k_{i \rightarrow j} P_i(t) + \sum_j k_{j \rightarrow i} P_j(t)$$

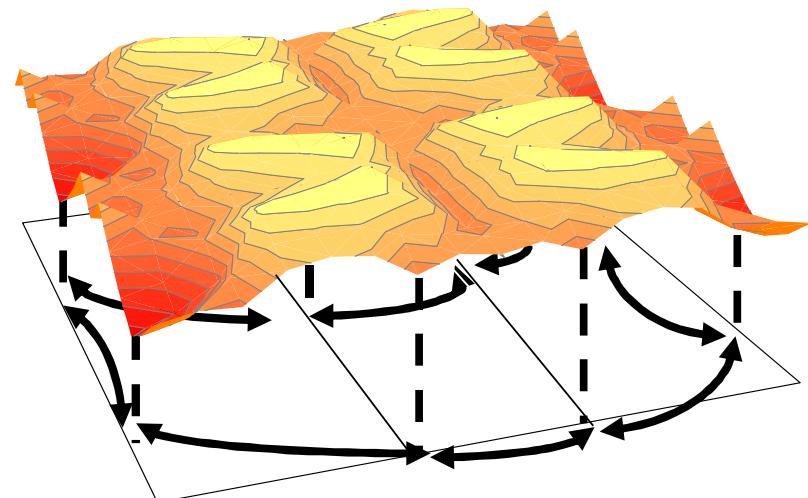


2) Process rates

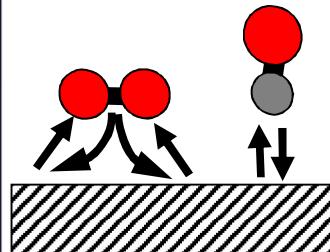
PES accuracy
Reaction rate theory

1) Elementary processes

Fixed process list vs. „on-the-fly“ kMC
Lattice vs. off-lattice kMC

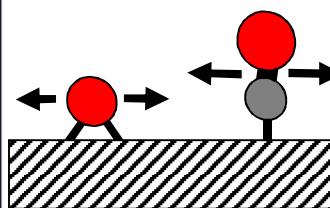


Monte Carlo sampling - applications



Adsorption:

CO - unimolecular, O₂ – dissociative
no barrier
rate given by impingement $k \approx S_0 p / (2\pi m k_B T)$

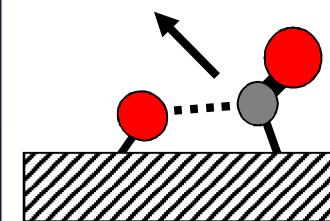


Desorption:

CO – 1st order, O₂ – 2nd order
out of DFT adsorption well (= barrier)
prefactor from detailed balance

Diffusion:

hops to nearest neighbor sites
site and element specific
barrier from DFT (TST)
prefactor from DFT (hTST)



Reaction:

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

26 elementary processes
considered

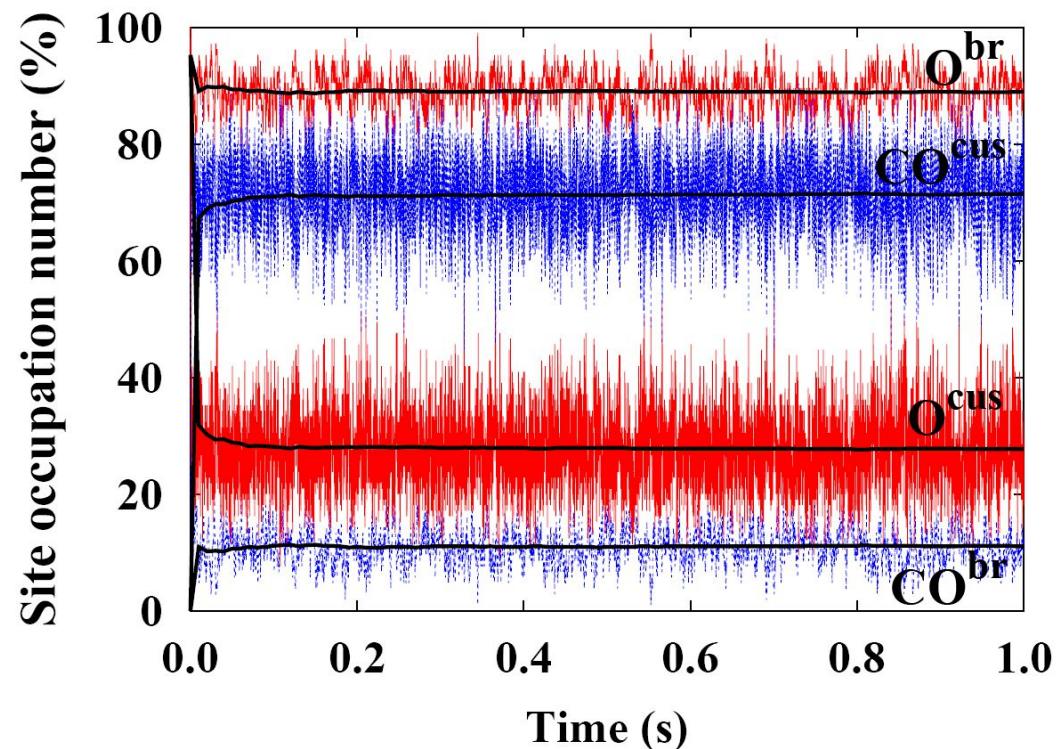
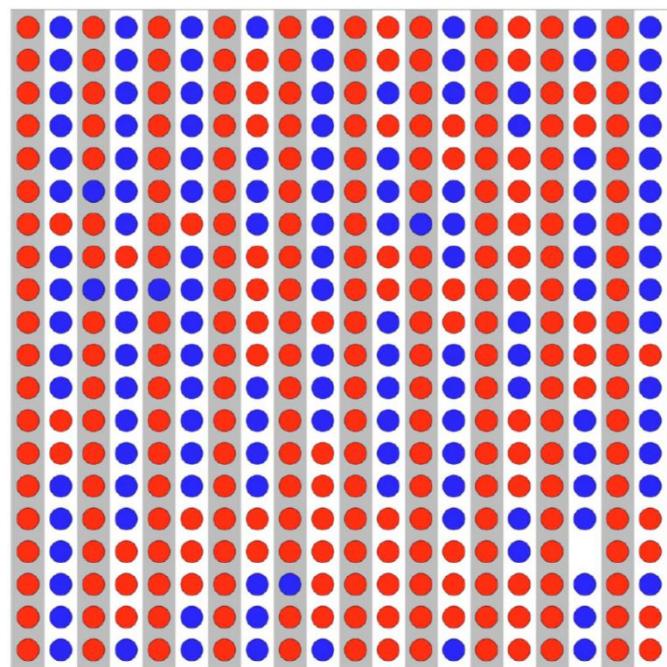
K. Reuter and M. Scheffler, Phys. Rev. B 73, 045433 (2006)

Monte Carlo sampling - applications

$T = 600 \text{ K}$

$p_{\text{O}_2} = 1 \text{ atm}$

$p_{\text{CO}} = 7 \text{ atm}$

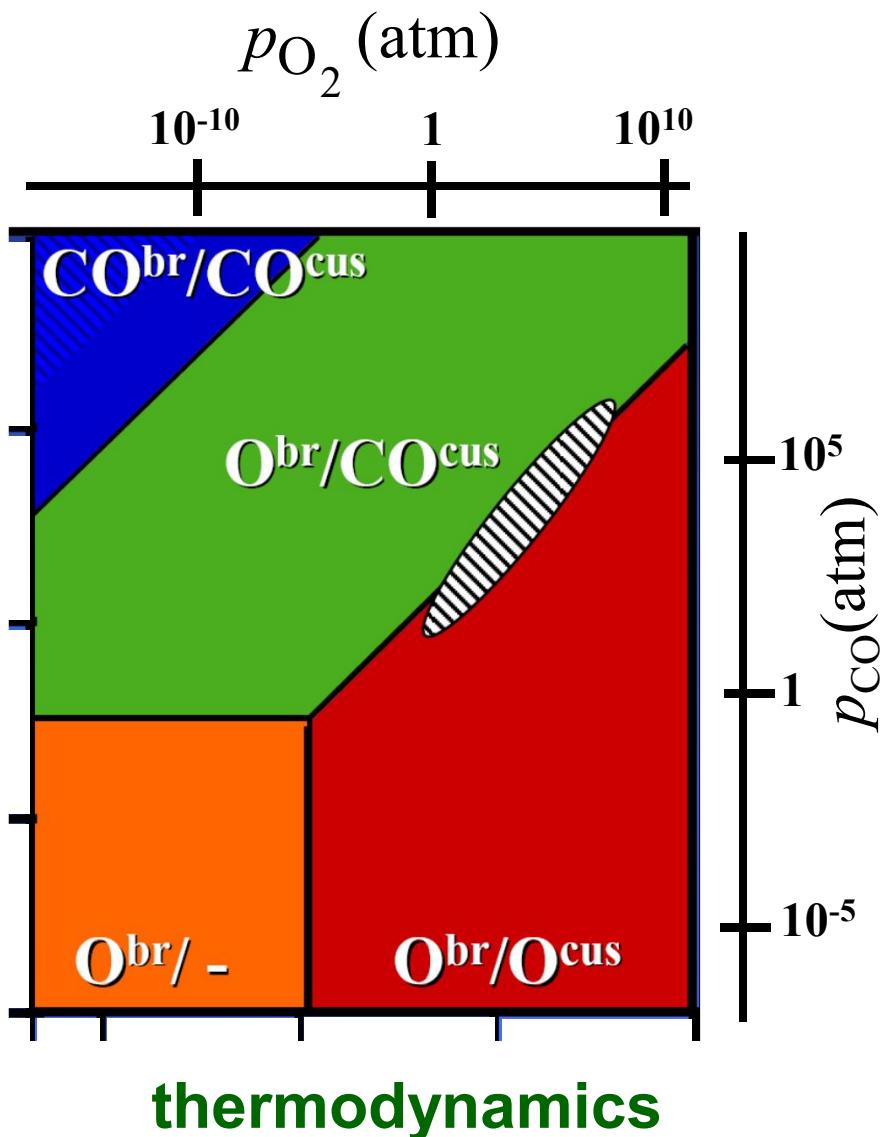
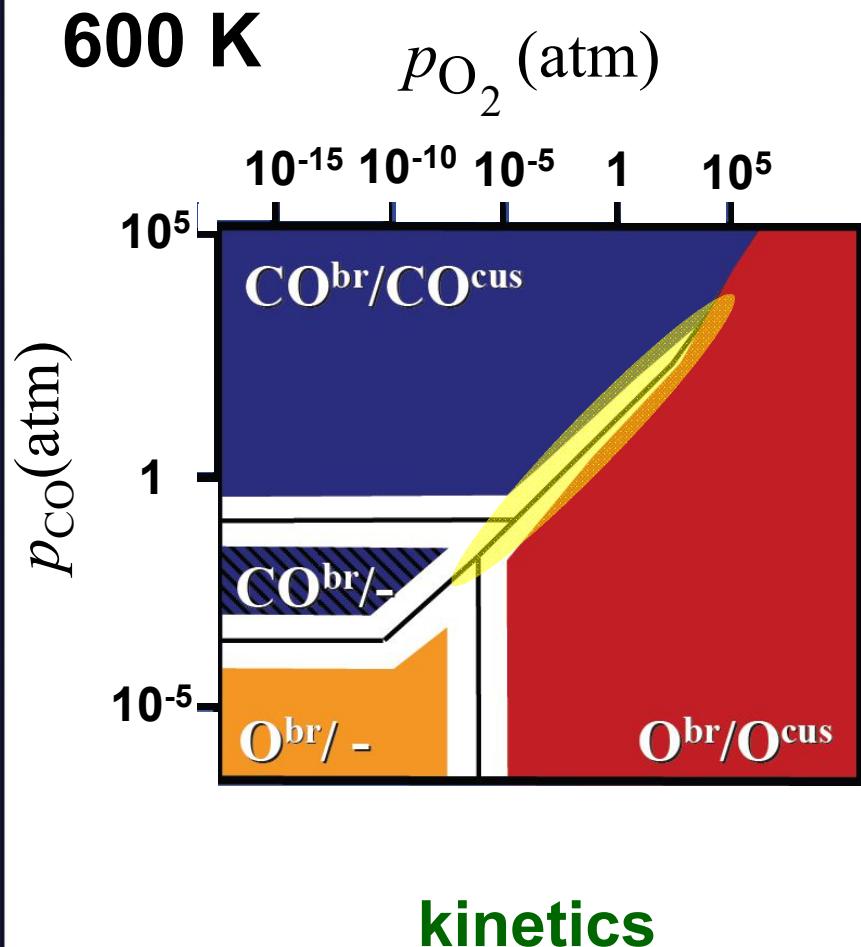


K. Reuter, D. Frenkel and M. Scheffler, Phys. Rev. Lett. 93, 116105 (2004)

K. Reuter, C. Stampfl, and M. Scheffler, Handbook of materials modeling, part A. Methods, p. 149, Springer, Berlin (2005)

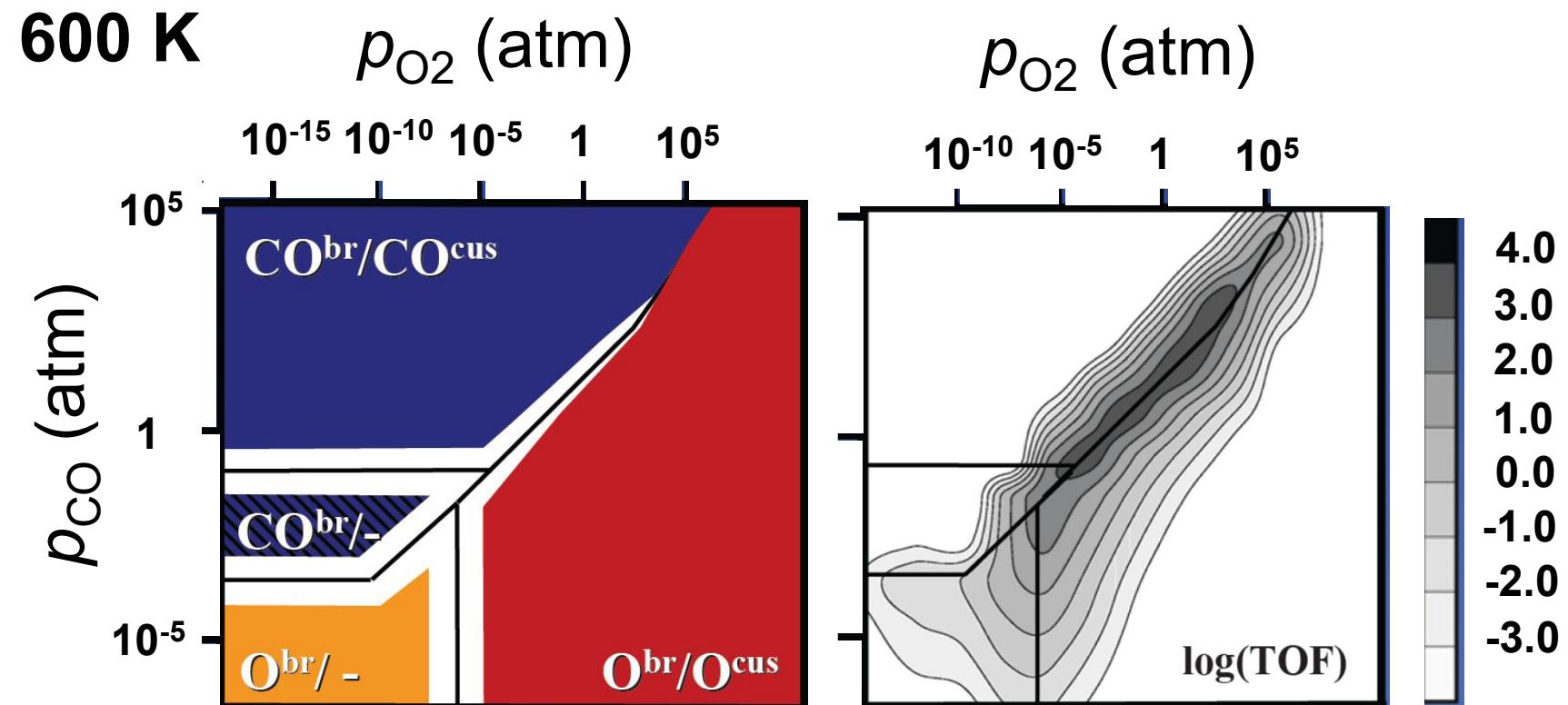
Monte Carlo sampling - applications

kMC phase diagrams



Monte Carlo sampling - applications

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



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

Summary

- ***Ab initio* atomistic thermodynamics approach allows to model materials in thermodynamic equilibrium at realistic temperatures and pressures from first principles**
- **Surface phase diagrams and defect concentrations as a function of temperature and pressure are two prominent examples**
- **Machine learning provides means for fast configuration sampling using coarse-grained models, in particular for alloys and surfaces**

The End ...