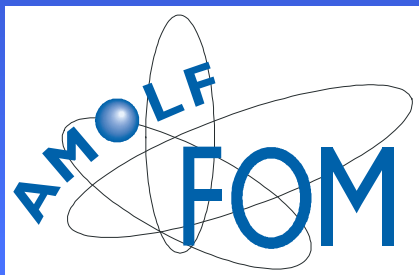


First-principles atomistic thermodynamics

(and its application in heterogeneous catalysis)



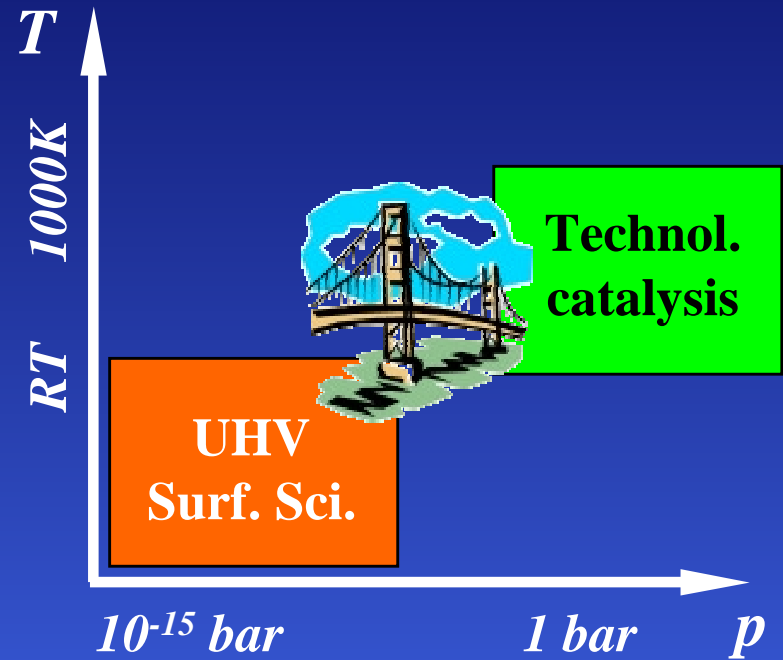
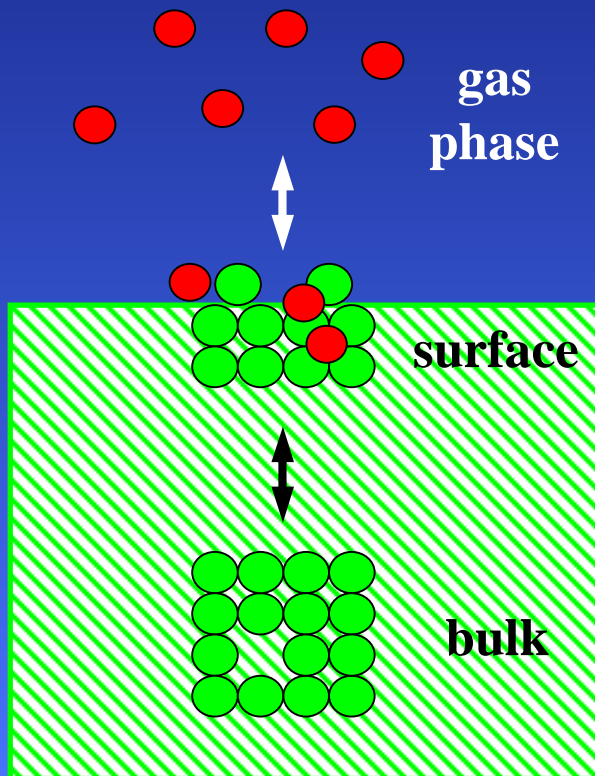
Karsten Reuter

Fritz-Haber-Institut, Berlin

AMOLF, Amsterdam

Motivation

- Extend the length scale
- Consider finite temperature effects



I. Connecting thermodynamics, statistical mechanics and density functional theory

Statistical Mechanics,
D.A. McQuarrie, Harper Collins Publ. (1976)

Introduction to Modern Statistical Mechanics,
D. Chandler, Oxford Univ. Press (1987)

M. Scheffler in *Physics of Solid Surfaces 1987,*
J. Koukal (Ed.), Elsevier (1988)



Thermodynamics in a nutshell

| | |
|-------------------------|--------------------------------------|
| Internal energy (U) | $E^{\text{tot}}(S, V)$ |
| Enthalpy | $H(S, p) = E^{\text{tot}} + pV$ |
| (Helmholtz) free energy | $F(T, V) = E^{\text{tot}} - TS$ |
| Gibbs free energy | $G(T, p) = E^{\text{tot}} - TS + pV$ |

Potential functions

- Equilibrium state of system minimizes corresponding potential function
- In its set of variables the total derivative of each potential function is simple (derive from 1st law of ThD: $dE^{\text{tot}} = dQ + dW$, $dW = -pdV$, $dQ = TdS$)

$$dE = TdS - pdV$$

$$dH = TdS + Vdp$$

$$dF = -SdT - pdV$$

$$dG = -SdT + Vdp$$

⇒ These expressions open the gate to a whole set of general relations like:

$$S = -(\partial F/\partial T)_V, p = -(\partial F/\partial V)_T$$

$$E^{\text{tot}} = -T^2 (\partial/\partial T)_V (F/T) \quad \text{Gibbs-Helmholtz eq.}$$

$$(\partial T/\partial V)_S = -(\partial p/\partial S)_V \text{ etc. Maxwell relations}$$

- Chemical potential $\mu = (\partial G/\partial n)_{T,p}$ is the cost to remove a particle from the system.
Homogeneous system: $\mu = G/N (= g)$
i.e. Gibbs free energy per particle



Link to statistical mechanics

A many-particle system will flow through its huge phase space, fluctuating through all microscopic states consistent with the constraints imposed on the system. For an isolated system with fixed energy E and fixed size V, N (microcanonic ensemble) these microscopic states are all equally likely at thermodynamic equilibrium (i.e. equilibrium is the most random situation).

- Partition function $Z = Z(T, V) = \sum_i \exp(-E_i / k_B T) \Rightarrow$ Boltzmann-weighted sum over all possible fluctuations
 $\Rightarrow F = -k_B T \ln(Z)$

- If groups of degrees of freedom are decoupled from each other (i.e. if the energetic states of one group do not depend on the state within the other group), then

$$Z_{\text{total}} = \left(\sum_i \exp(-E_i^A / k_B T) \right) \left(\sum_i \exp(-E_i^B / k_B T) \right) = Z^A Z^B$$

$$\Rightarrow F_{\text{total}} = F^A + F^B$$

e.g. electronic \leftrightarrow nuclear (Born-Oppenheimer)
rotational \leftrightarrow vibrational



- N indistinguishable, independent particles: $Z_{\text{total}} = 1/N! \left(Z_{\text{one particle}} \right)^N$

Computation of free energies: ideal gas I

$$Z = 1/N! \left(\cancel{Z_{\text{nucl}}} Z_{\text{el}} Z_{\text{trans}} Z_{\text{rot}} Z_{\text{vib}} \right)^N$$

$$\Rightarrow \mu(T,p) = G / N = (F + pV) / N = (-k_B T \ln(Z) + pV) / N$$

i) Electr. free energy $Z_{\text{el}} = \sum_i \exp(-E_i^{\text{el}} / k_B T)$

$$\Rightarrow F_{\text{el}} \approx E^{\text{tot}} - k_B T \ln(I_{\text{spin}})$$

Typical excitation energies eV $\gg k_B T$, only (possibly degenerate) ground state contributes significantly

Required input:

Internal energy E^{tot}

Ground state spin degeneracy I_{spin}

ii) Transl. free energy $Z_{\text{trans}} = \sum_{\underline{k}} \exp(-\hbar^2 k^2 / 2mk_B T)$

Particle in a box of length $L = V^{1/3}$

$$(L \rightarrow \infty) \Rightarrow Z_{\text{trans}} \approx V (2\pi mk_B T / \hbar^2)^{3/2}$$

Required input:

Particle mass m



Computation of free energies: ideal gas II

iii) Rotational free energy $Z_{\text{rot}} = \sum_J (2J+1) \exp(-J(J+1)B_0 / k_B T)$ Rigid rotator

(Diatomic molecule) $\Rightarrow Z_{\text{rot}} \approx -k_B T \ln(k_B T / \sigma B_0)$ $\sigma = 2$ (homonucl.), $= 1$ (heteronucl.)
 $B_0 \sim m d^2$ (d = bond length)

Required input: Rotational constant B_0
 (exp: tabulated microwave data)

iv) Vibrational free energy $Z_{\text{vib}} = \sum_{i=1}^M \sum_n \exp(-(n + 1/2)\omega_i / k_B T)$ Harmonic oscillator

$\Rightarrow \mu_{\text{vib}}(T) = \sum_{i=1}^M \frac{1}{2} \omega_i + k_B T \ln(1 - \exp(-\omega_i / k_B T))$

Required input: M fundamental vibr. modes ω_i



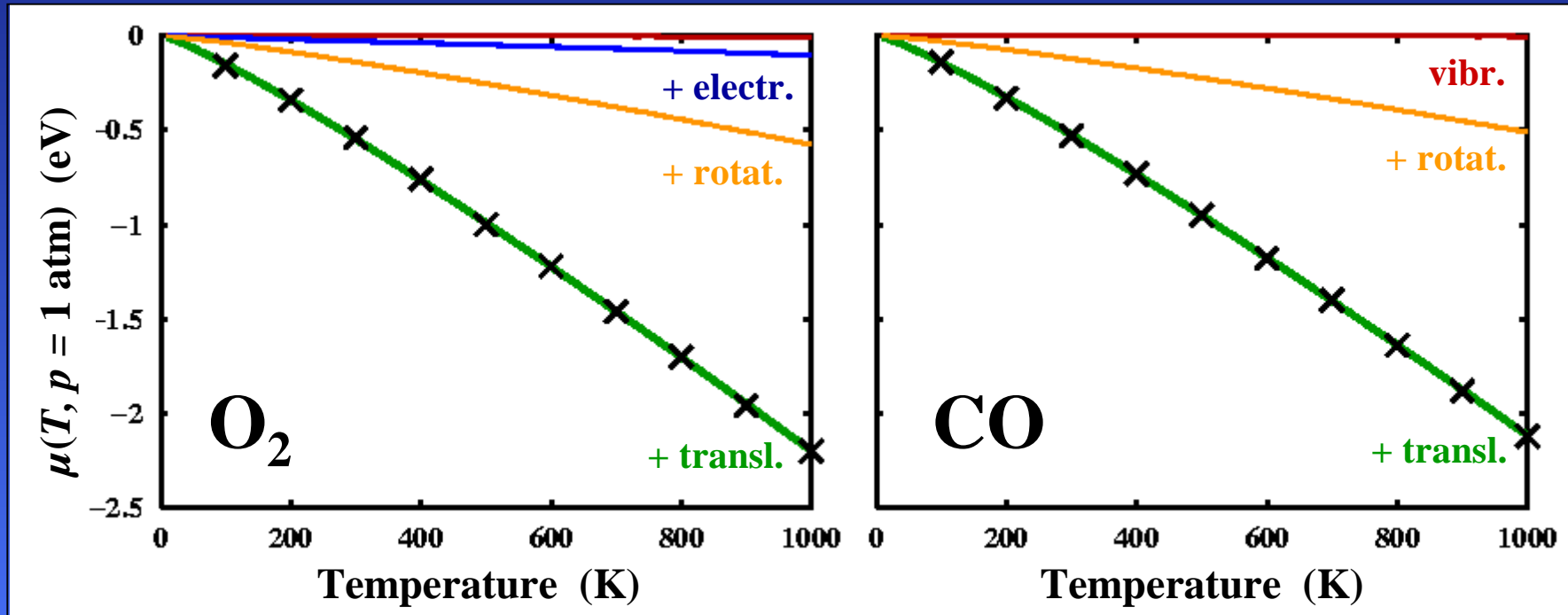
Calculate dynamic matrix $D_{ij} = (m_i m_j)^{-1/2} (\partial^2 E^{\text{tot}} / \partial r_i \partial r_j)_{r_{\text{eq}}}$
 Solve eigenvalue problem $\det(\mathbf{D} - \mathbf{1} \omega_i^2)$



Computation of free energies: ideal gas III

| | | O ₂ | CO |
|------------------------|-------|----------------|------|
| m | (amu) | 32 | 28 |
| ν_{stretch} | (meV) | 196 | 269 |
| B_0 | (meV) | 0.18 | 0.24 |
| σ | | 2 | 1 |
| I_{spin} | | 3 | 1 |

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



Alternatively:

$$\mu(T, p) = \mu(T, p^0) + kT \ln(p/p^0)$$

and $\mu(T, p^0 = 1 \text{ atm})$ tabulated in thermochem. tables (e.g. JANAF)

Computation of free energies: solids

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

F^{trans} Translational free energy
 F^{rot} Rotational free energy } $\propto 1/M \rightarrow 0$

pV $V = V(T,p)$ from equation of state, varies little $\rightarrow 0$ for $p < 100$ atm

F^{conf} Configurational free energy \rightarrow depends on application

E^{tot} Internal energy \rightarrow DFT

F^{vib} Vibrational free energy \rightarrow phonon band structure

$E^{\text{tot}}, F^{\text{vib}}$ use differences
use simple models to approx. F^{vib} (Debye, Einstein)

\Rightarrow Solids (low T): $G(T,p) \sim E^{\text{tot}} + F^{\text{conf}}$



II. Equilibrium concentration of point defects:

O dissolution in ruthenium

Solid State Physics,

N.W. Ashcroft and N.D. Mermin, Holt-Saunders (1976)

K. Reuter *et al.*, Phys. Rev. B 65, 165403 (2002)



Isolated point defects and bulk dissolution

On entropic grounds there will always be a finite concentration of defects at finite temperature, even though the creation of a defect costs energy ($E_D > 0$).

How large is it?

Internal energy:

$$E^{\text{tot}} = n E_D$$

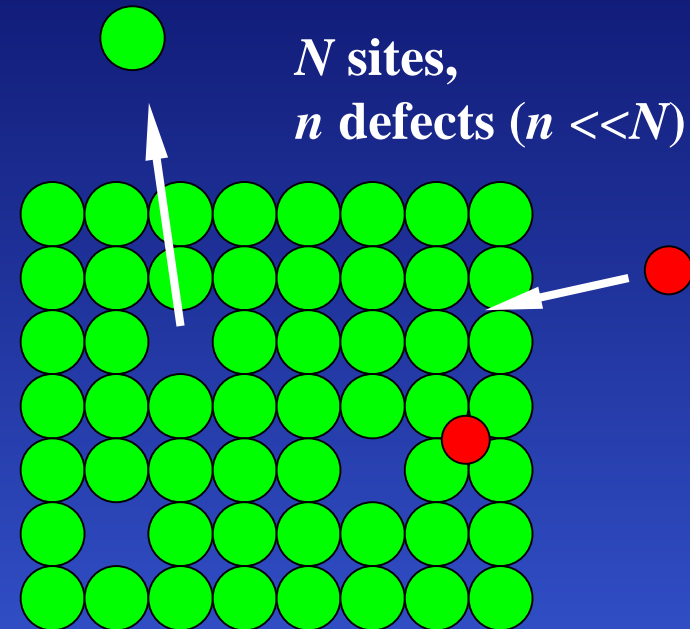
Config. entropy:

$$TS^{\text{conf}} = k_B T \ln Z(n)$$

$$\text{with } Z = \frac{N(N-1)\dots(N-n+1)}{1\cdot 2\cdot \dots\cdot n} = \frac{N!}{(N-n)!n!}$$

Minimize free energy:

$$(\partial G/\partial n)_{T,p} = \partial/\partial n_{T,p} (E^{\text{tot}} - TS^{\text{conf}} + pV) = 0$$



Forget pV , use Stirling: $\ln N! \approx N(\ln N - 1) \Rightarrow$

$$n/N = \exp(-E_D/k_B T)$$

Oxygen dissolution in bulk ruthenium

In an oxygen-rich atmosphere,
how much O dissolves in bulk Ru?

O in octahedral interstitial site (DFT):

$E_D \approx +1.25$ eV (with respect to free O₂)

$$n/N = \exp(-E_D/k_B T)$$

$\sim 10^{23}$ sites/cm³ \Rightarrow ~ 20 O atoms/cm³ (RT)
 $\sim 10^{14}$ O atoms/cm³ (800K)

With $\sim 10^{15}$ sites/cm², this still
only amounts to about 0.1 ML
even at $T = 800$ K...



II. Effect of a surrounding gas phase on the surface structure and composition:

$\text{RuO}_2(110)$ in an oxygen atmosphere

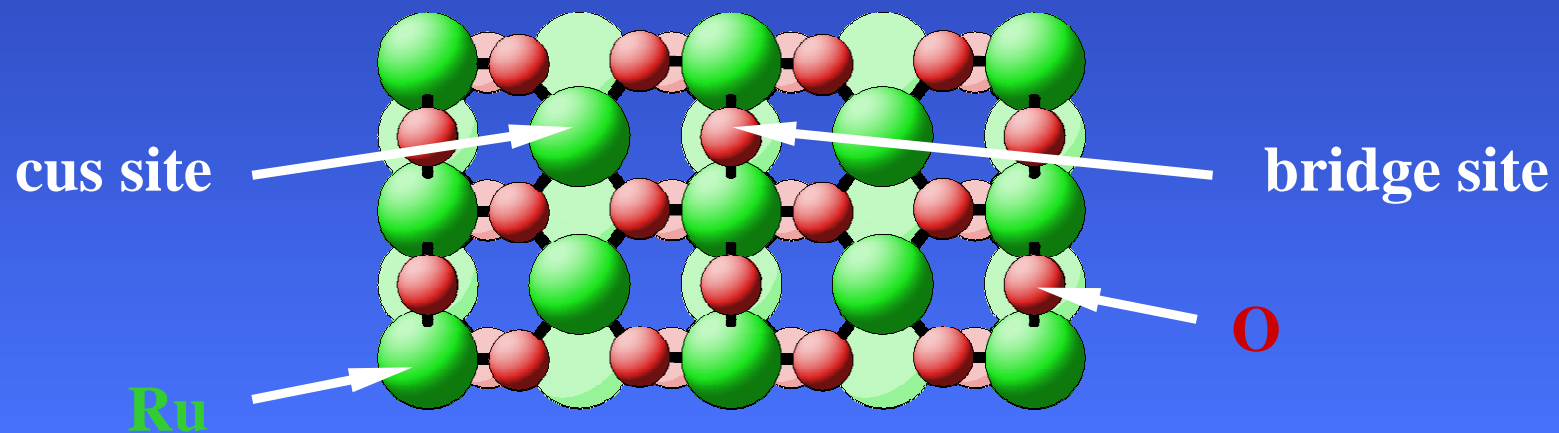
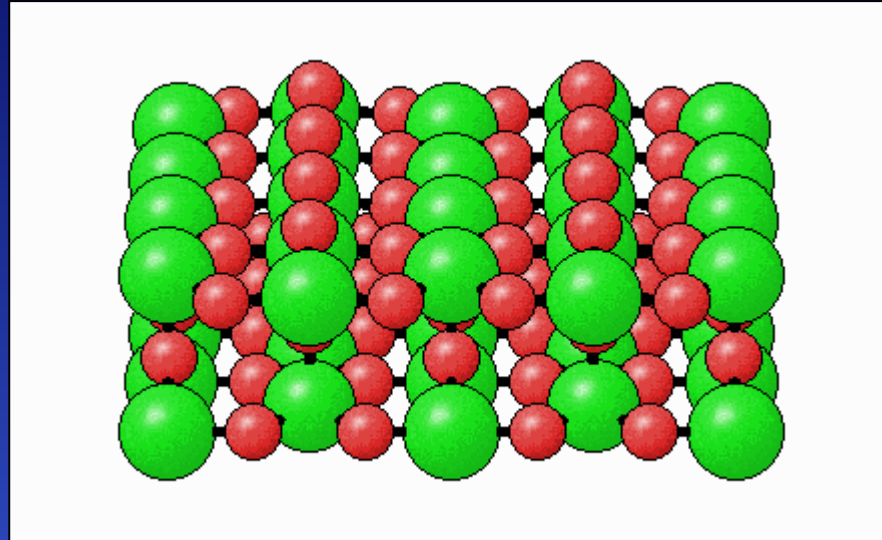
E. Kaxiras *et al.*, Phys. Rev. B 35, 9625 (1987)

X.-G. Wang *et al.*, Phys. Rev. Lett. 81, 1038 (1998)

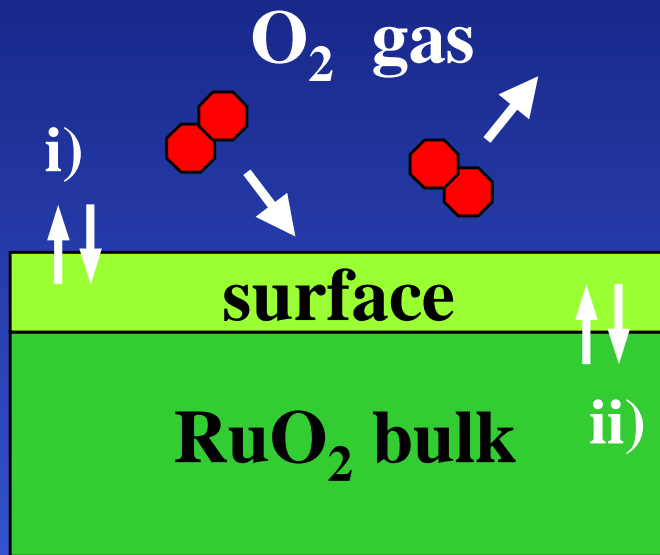
K. Reuter and M. Scheffler, Phys. Rev. B 65, 035406 (2002)



RuO₂(110): the active phase in CO oxidation over Ru(0001)



Influence of the environment on surface structure and stoichiometry



$$\text{i) } \gamma_{\text{surf.}} = 1/A (G_{\text{RuO}_2}^{\text{surf.}} - N_{\text{O}} \mu_{\text{O}} - N_{\text{Ru}} \mu_{\text{Ru}})$$

$$\text{ii) } \mu_{\text{Ru}} + 2 \mu_{\text{O}} = g_{\text{RuO}_2}^{\text{bulk}}$$

$$\Rightarrow \chi(T,p) = 1/A [G_{\text{RuO}_2}^{\text{surf.}}(T,p) - N_{\text{Ru}} g_{\text{RuO}_2}^{\text{bulk}}(T,p) + (2N_{\text{Ru}} - N_{\text{O}}) \mu_{\text{O}}]$$



$$\chi(T,p) \approx (\Delta E^{\text{tot}} - \Delta F^{\text{vib}})/A + (2N_{\text{Ru}} - N_{\text{O}}) \mu_{\text{O}}/A$$

Reasonable gas phase limits

Low O concentration: oxygen leaves solid, formation of Ru crystallites

$$\left. \begin{array}{l} \mu_{\text{Ru}} < g_{\text{Ru}}^{\text{bulk}}(T,p) \\ \mu_{\text{Ru}} + 2\mu_{\text{O}} = g_{\text{RuO}_2}^{\text{bulk}}(T,p) \end{array} \right\} \mu_{\text{O}} > \frac{1}{2} (g_{\text{RuO}_2}^{\text{bulk}}(T,p) - g_{\text{Ru}}^{\text{bulk}}(T,p))$$

$$\text{O-poor limit: } \mu_{\text{O}} \stackrel{!}{=} \frac{1}{2} (E_{\text{RuO}_2}^{\text{bulk}} - E_{\text{Ru}}^{\text{bulk}})$$

High O concentration: oxygen starts to “condense” on the surface

$$\text{O-rich limit: } \mu_{\text{O}} \stackrel{!}{=} \frac{1}{2} E_{\text{O}_2}^{\text{tot}}$$

⇒ Use $E_{\text{O}_2}^{\text{tot}}$ as reference zero: $\Delta\mu_{\text{O}} = \mu_{\text{O}} - \frac{1}{2}E_{\text{O}_2}^{\text{tot}}$

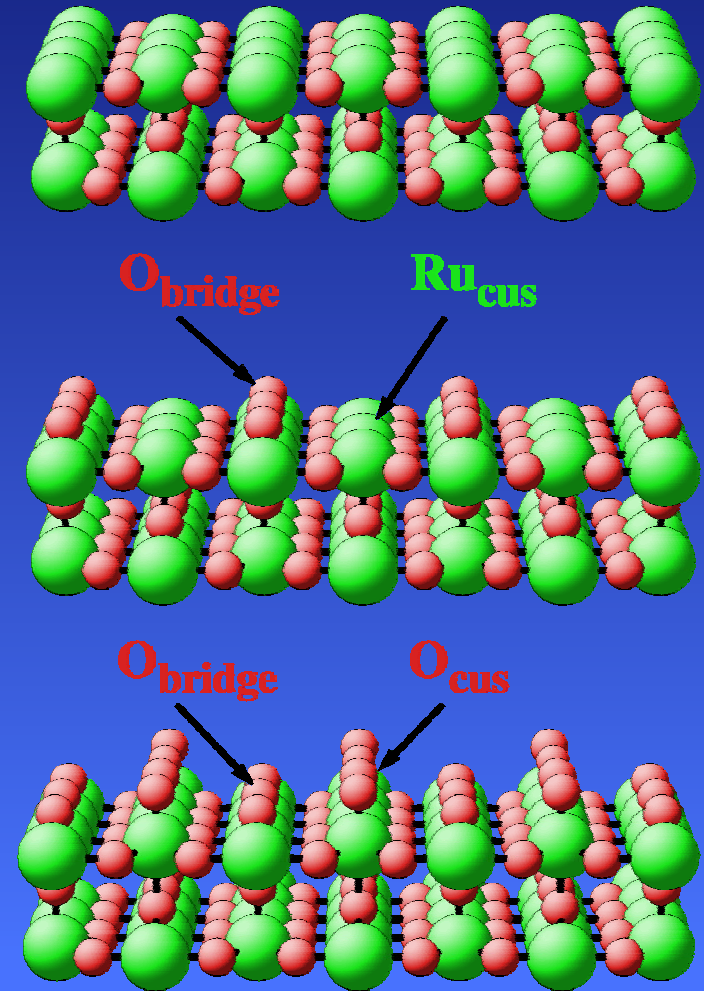
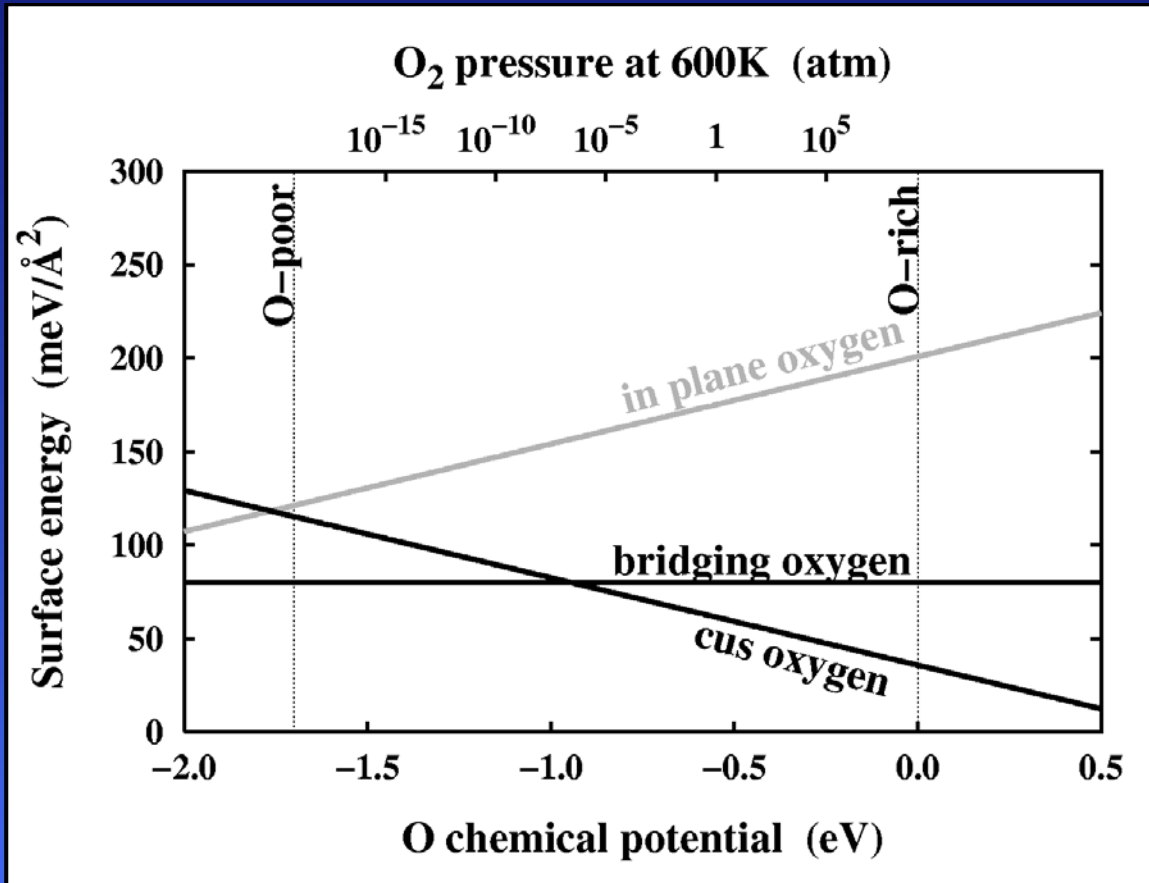
⇒ Introduce heat of formation at $T = 0\text{K}$: $\Delta G_f(0,0) = E_{\text{RuO}_2}^{\text{bulk}} - E_{\text{Ru}}^{\text{bulk}} - E_{\text{O}_2}^{\text{tot}}$



$$\frac{1}{2}\Delta G_f(0,0) < \Delta\mu_{\text{O}}(T,p) < 0$$

RuO₂(110) surface terminations

$$\chi(T,p) \approx \Delta E^{\text{tot}}/A + (2N_{\text{Ru}} - N_{\text{O}}) \mu_{\text{O}}/A$$

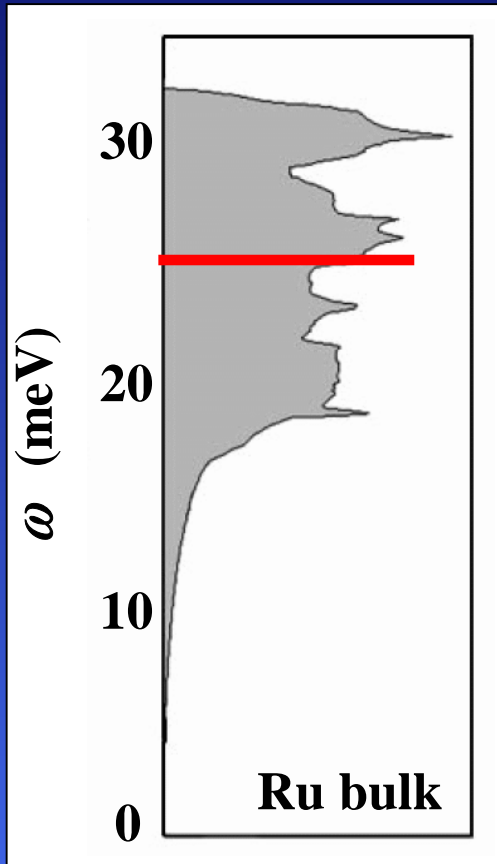


A high pressure termination !

Vibrational contributions to the surface free energy

$$F^{\text{vib}}(T, V) = \int d\omega F^{\text{vib}}(T, \omega) \sigma(\omega)$$

$$\begin{aligned} \Rightarrow \gamma^{\text{vib}} &= \Delta F^{\text{vib}}/A = \\ &= 1/A \int d\omega F^{\text{vib}}(T, \omega) \left[\sigma^{\text{surf.}}(\omega) - N_{\text{Ru}} \sigma_{\text{RuO}_2}^{\text{bulk}}(\omega) \right] \end{aligned}$$



R. Heid *et al.*,

Phys. Rev. B 61, 12059 (2000)



Only the vibrational changes at the surface contribute to the surface free energy

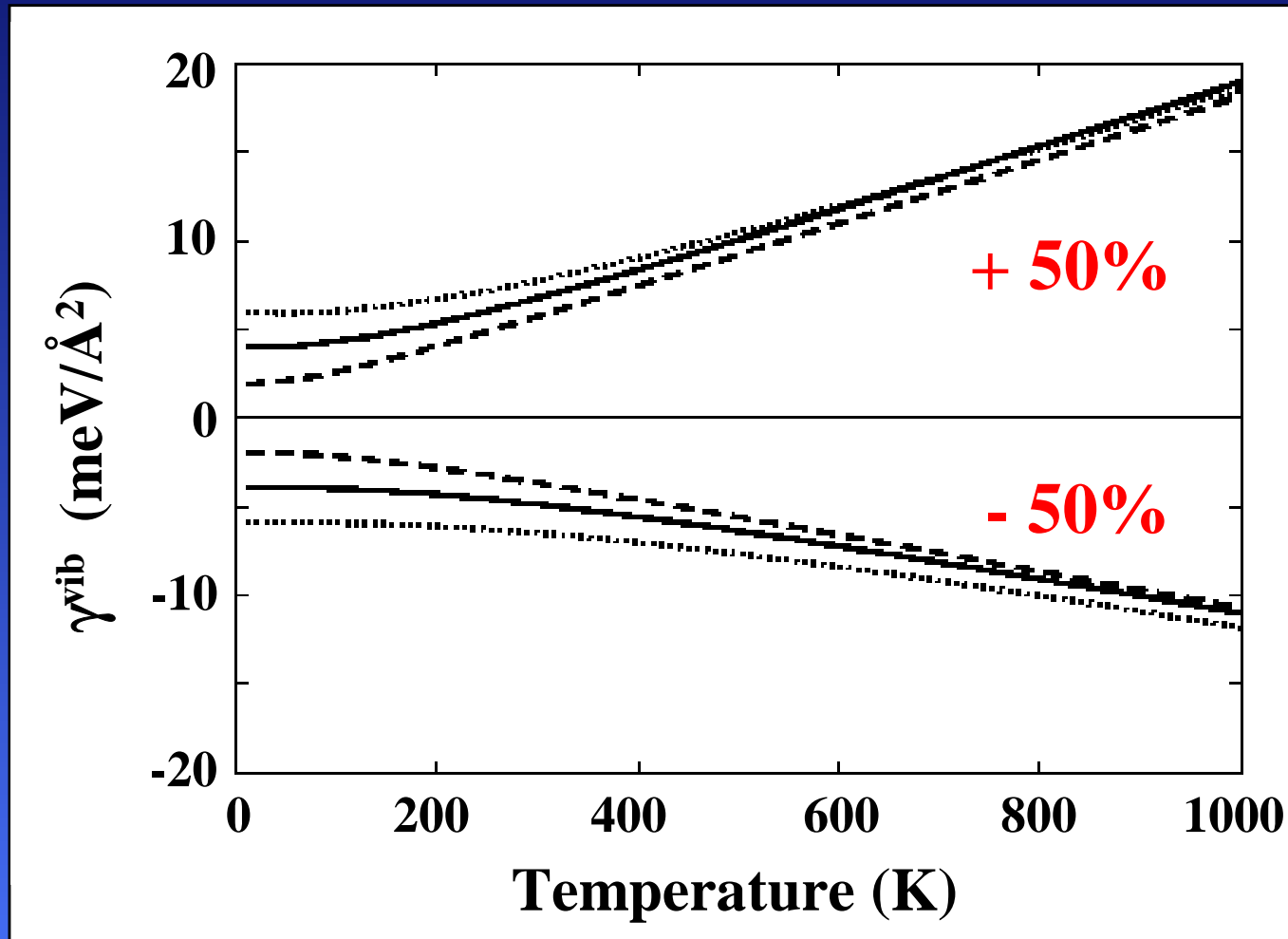
⇒ Use simple models for order of magnitude estimate

e.g. Einstein model: $\sigma(\omega) = \delta(\omega - \underline{\omega})$

$$\underline{\omega}_{\text{Ru}}(\text{bulk}) = 25 \text{ meV}$$

$$\underline{\omega}_{\text{O}}(\text{bulk}) = 80 \text{ meV}$$

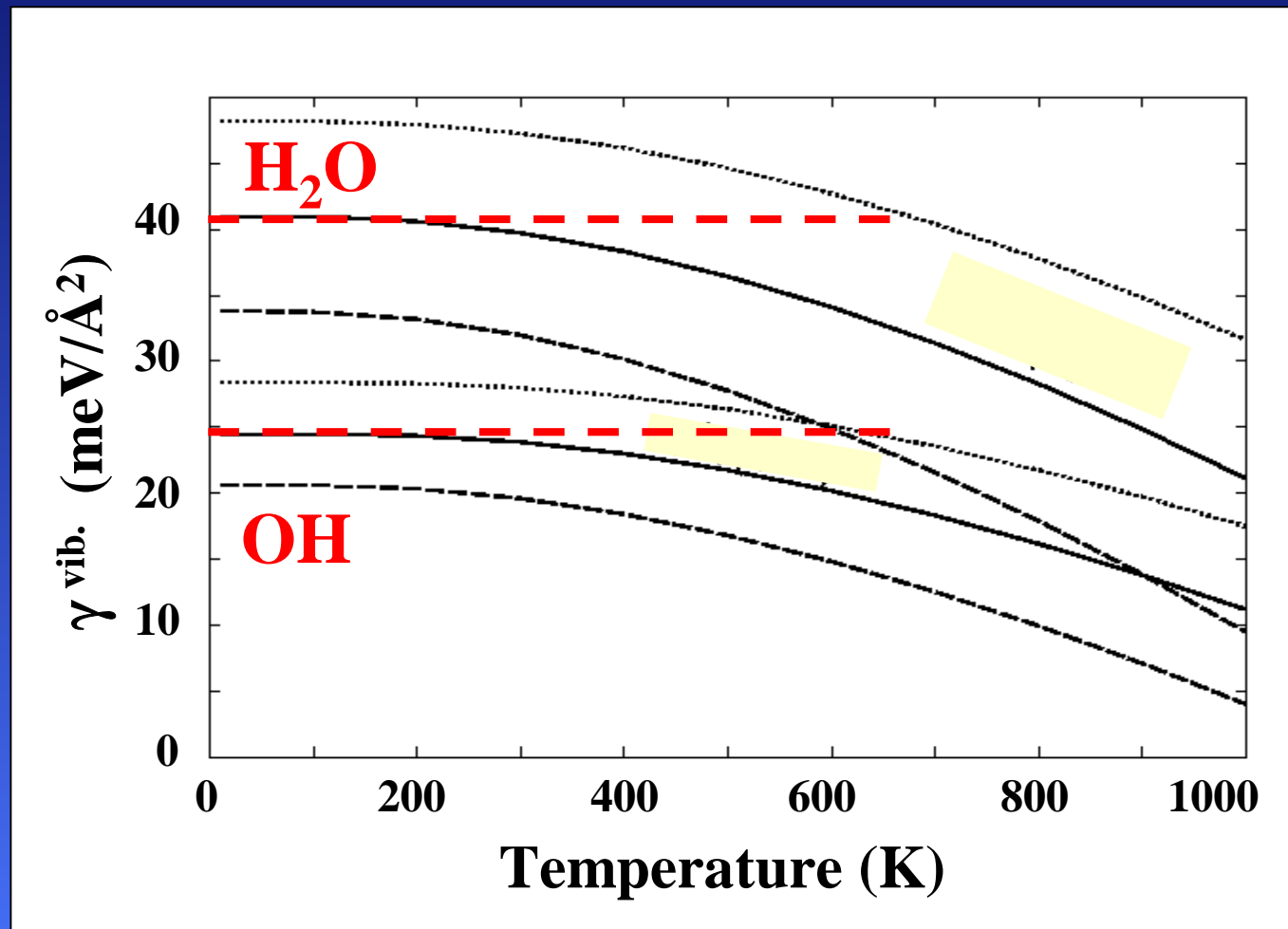
Surface induced variations of substrate modes



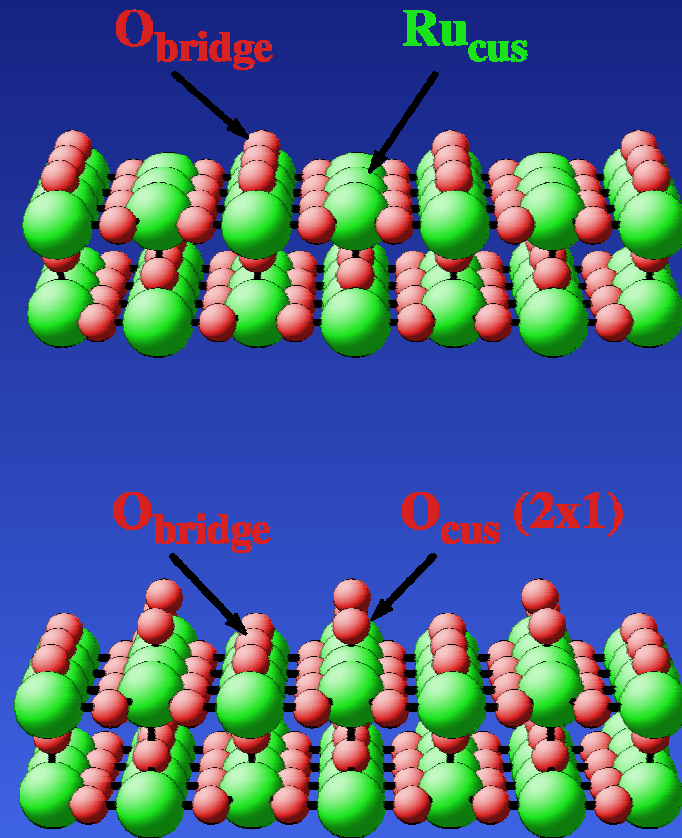
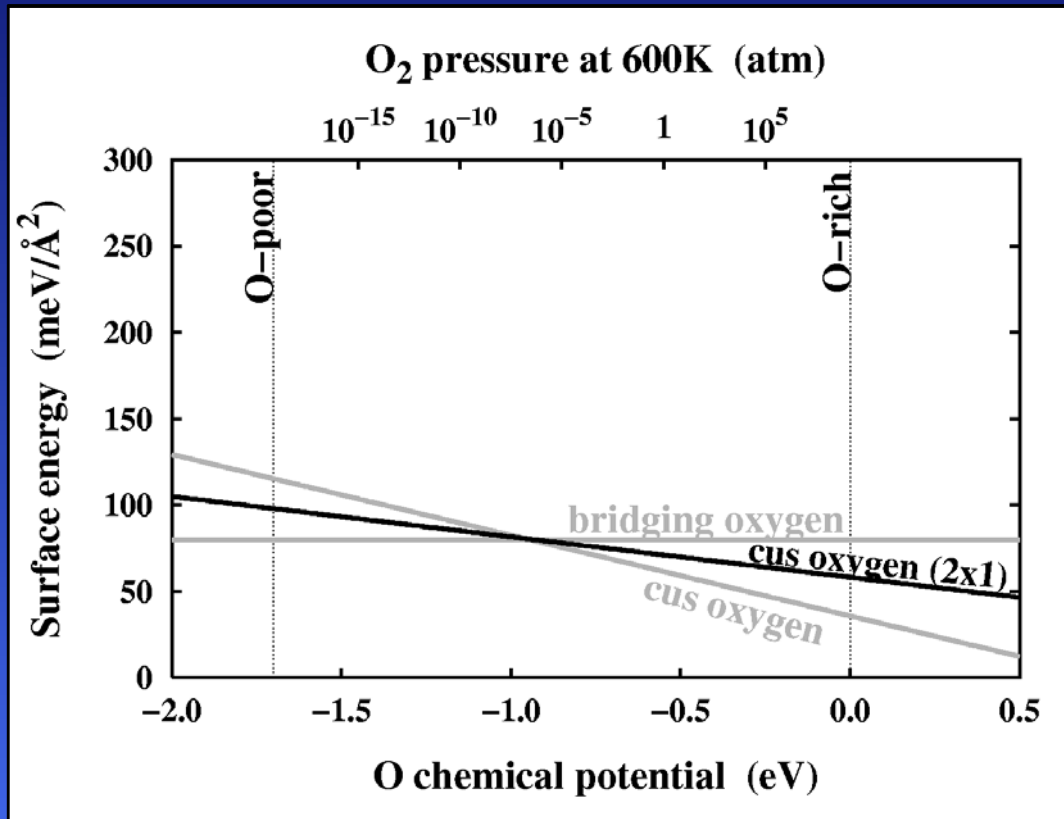
$< 10 \text{ meV}/\text{\AA}^2$ for $T < 600 \text{ K}$ - in this case!!!



Surface functional groups

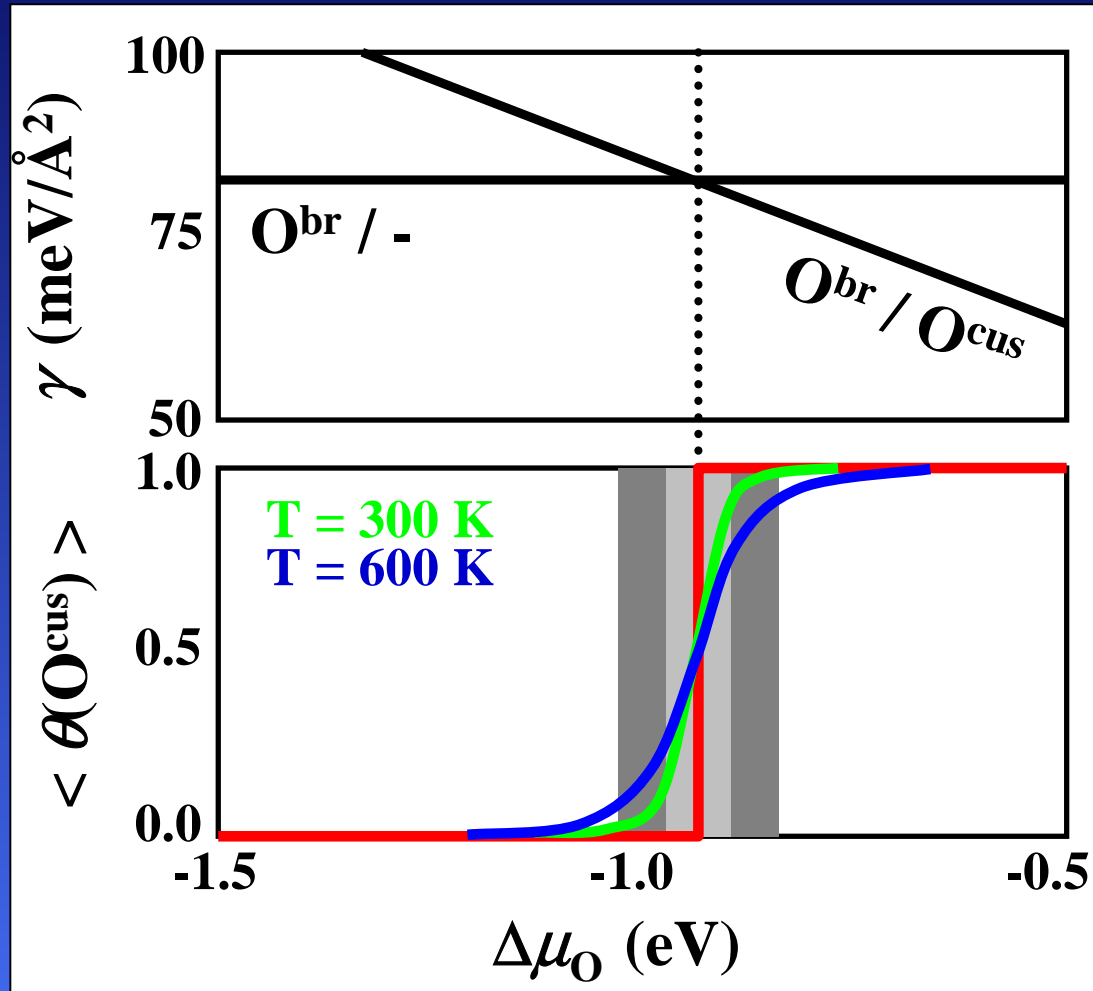


Lateral interactions and superstructures



No lateral interaction between O_{cus} atoms

Configurational entropy and phase transitions



$$TS^{\text{conf}} = k_B T \ln (N+n)! / (N!n!)$$

Stirling...

$$\Rightarrow TS^{\text{conf}}/A < 1.2 k_B T / A$$

for $\text{RuO}_2(110)$:

$$TS^{\text{conf}}/A < 5 \text{ meV}/\text{\AA}^2 \quad (T < 800\text{K})$$

Langmuir adsorption-isotherm
(no lateral interactions):

$$\langle \theta(\text{O}^{\text{cus}}) \rangle =$$

$$\frac{1}{1 + \exp((E^{\text{bind}} - \Delta\mu_{\text{O}})/k_B T)}$$



Configurational entropy smears out phase transitions

III. First-principles atomistic thermodynamics for oxidation catalysis

CO oxidation at $\text{RuO}_2(110)$

K. Reuter and M. Scheffler, *Phys. Rev. Lett.* 90, 046103 (2003)

K. Reuter and M. Scheffler, *Phys. Rev. B* 68, 045407 (2003)



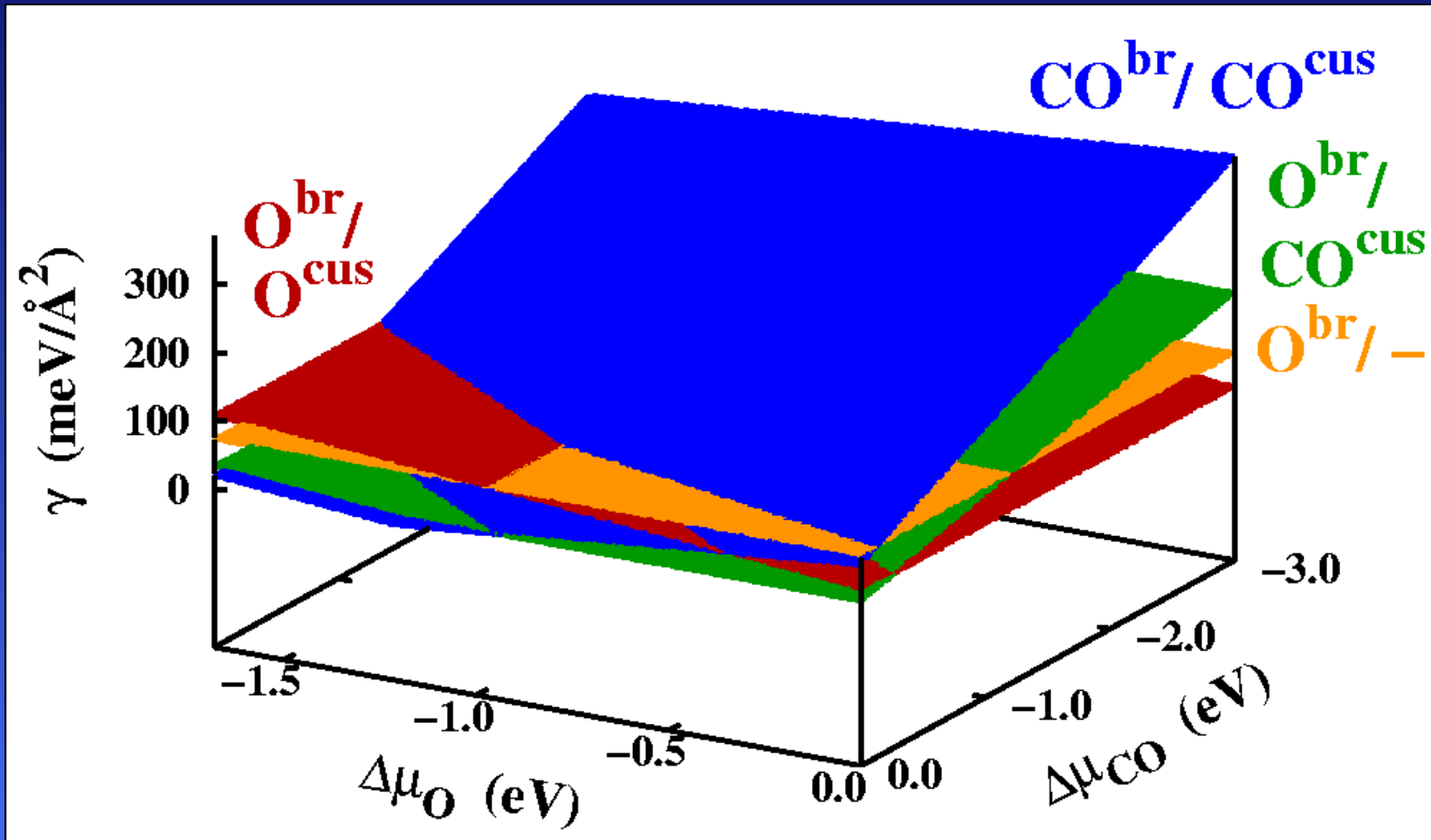
Treating a reactive multi-component environment



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

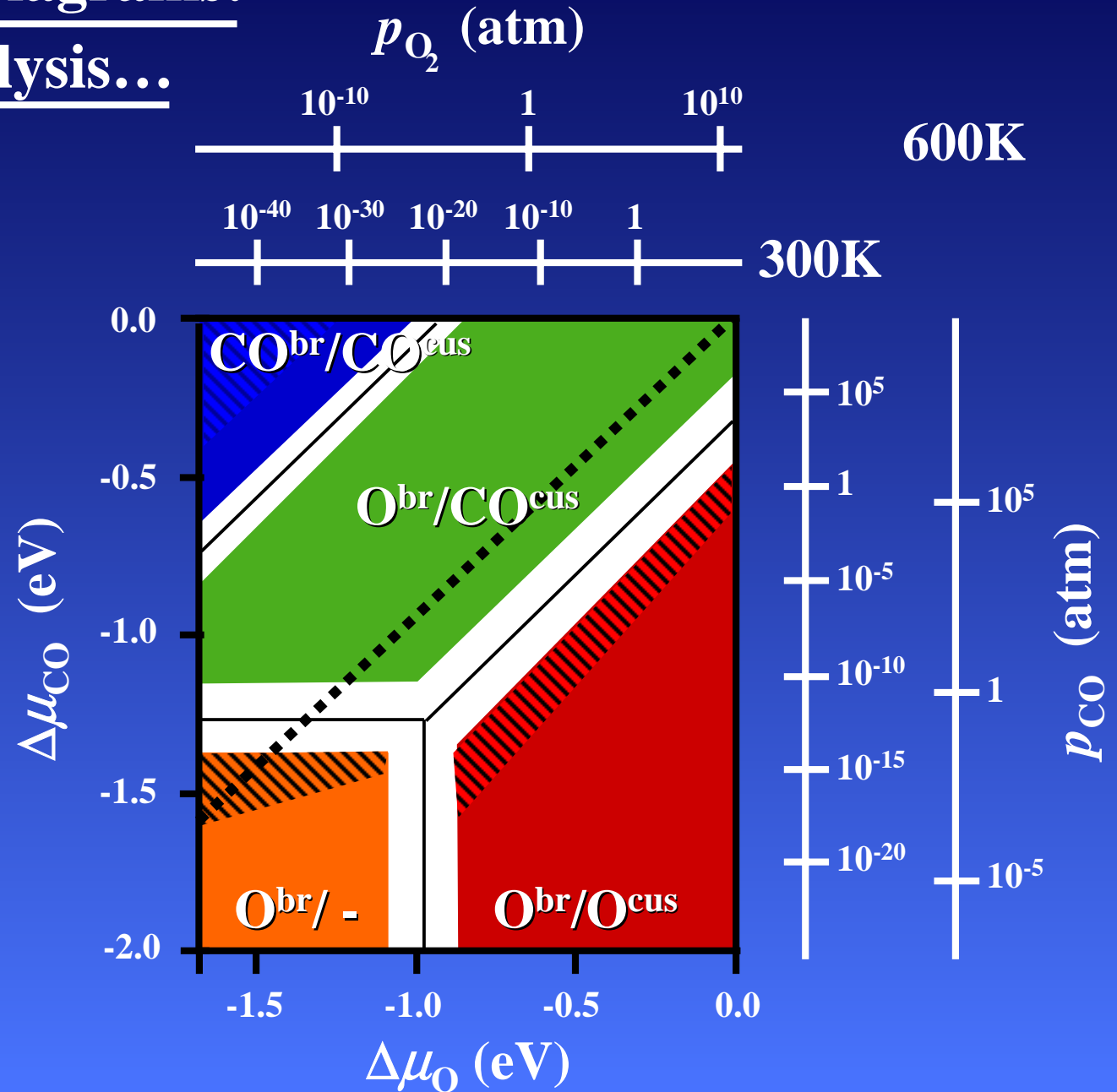


Surface free energy in a (O₂, CO) gas phase

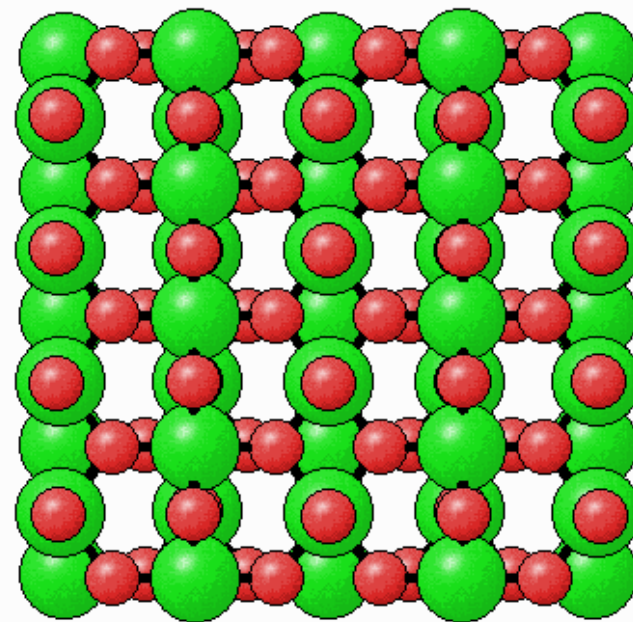
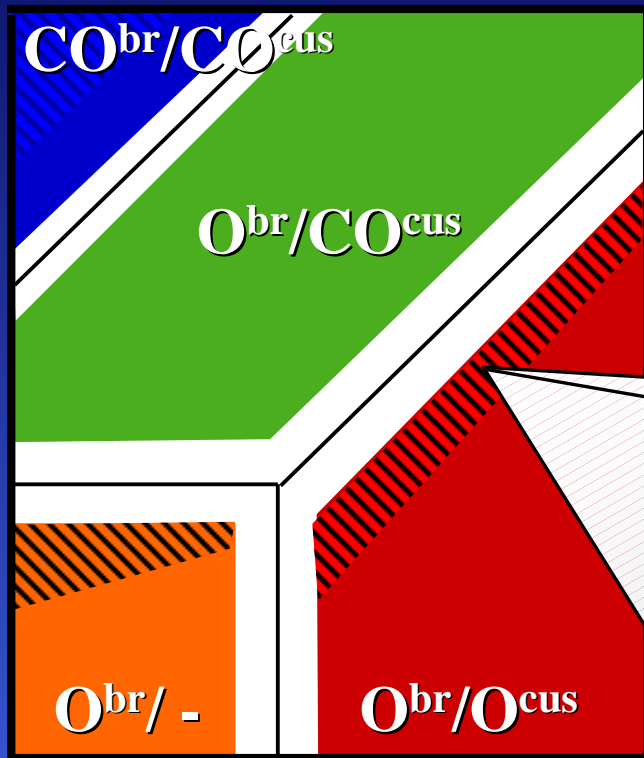


Surface phase diagrams:

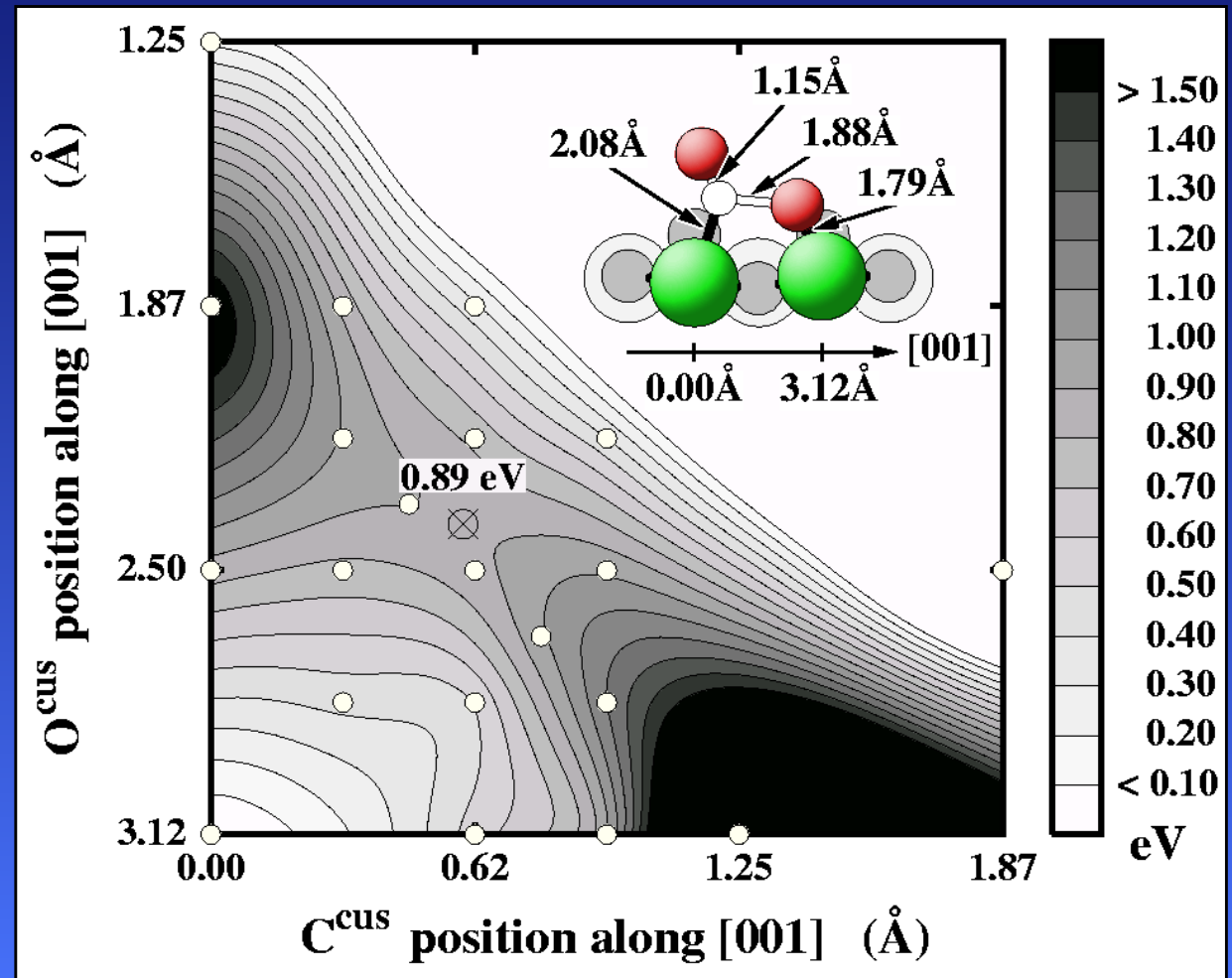
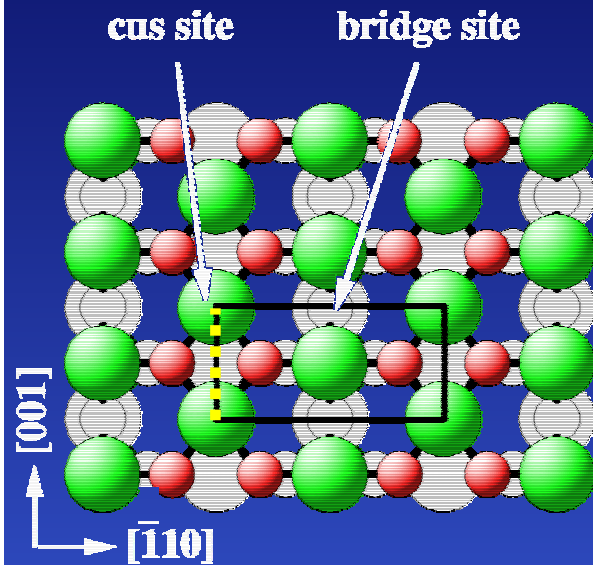
towards catalysis...



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



$\text{CO}^{\text{cus}} + \text{O}^{\text{cus}} \rightarrow \text{CO}_2$: Reaction barrier



Summary

Computation of free energies, concept of reservoirs

- allow any general thermodynamic reasoning
- main problem: V_{xc} vs. $k_B T$

Surfaces in finite gas phase

- surface structure and composition
(semiconductors, oxides, metals, oxide formation...)
- main problem: indirect, does not predict reconstructions

Application to catalysis

- “constrained equilibrium”
- identification of catalytically interesting regions
- main problem: kinetic effects
→ statistical mechanics (e.g. kMC)

