Ab Initio Thermodynamics and Heterogeneous Catalysis

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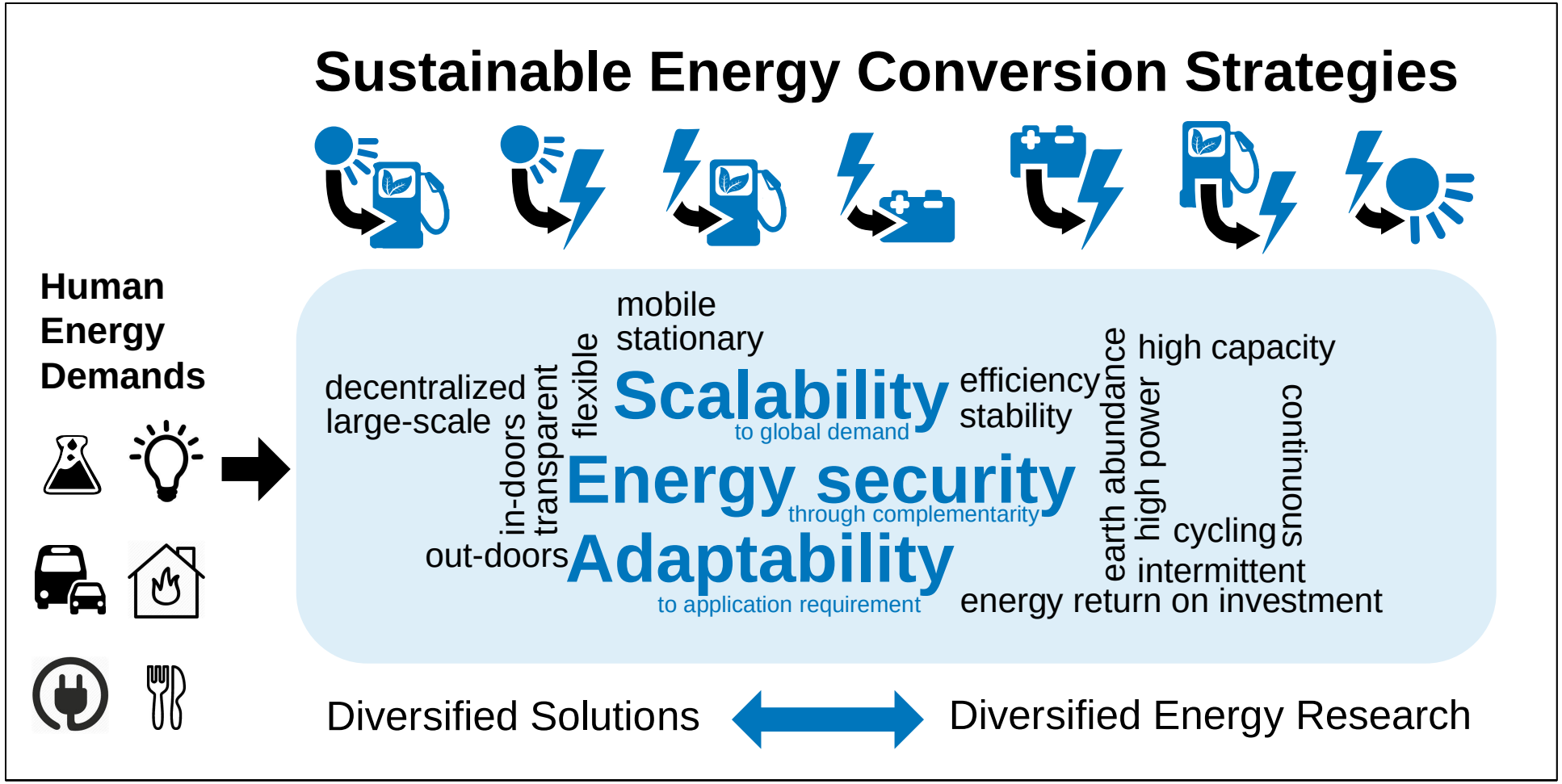
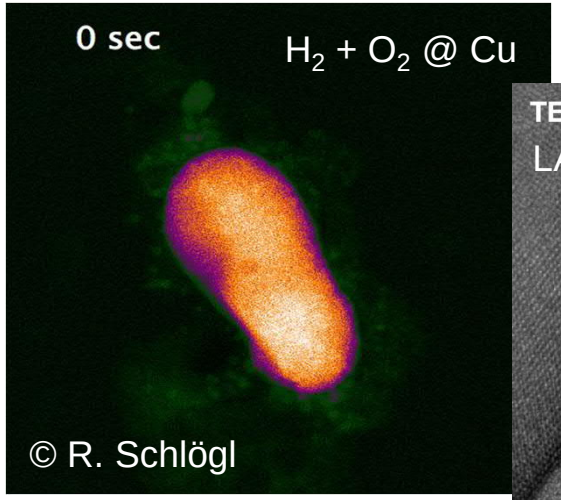
I. Motivation:

The need to extend the predictive realm of quantum chemistry

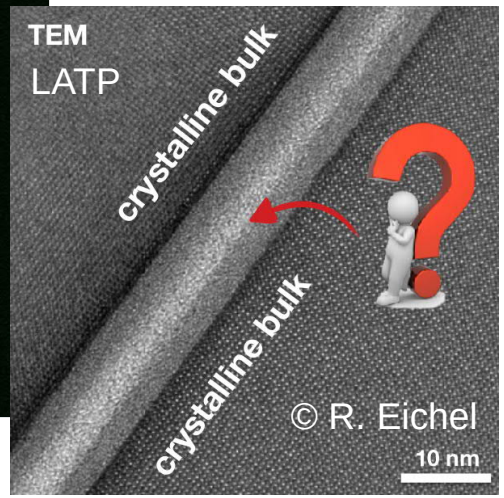
Sustainable Energy Conversion: The Engine of our Society

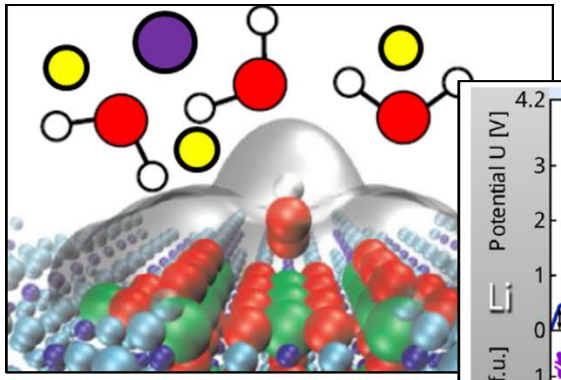


Interfacial Complexities

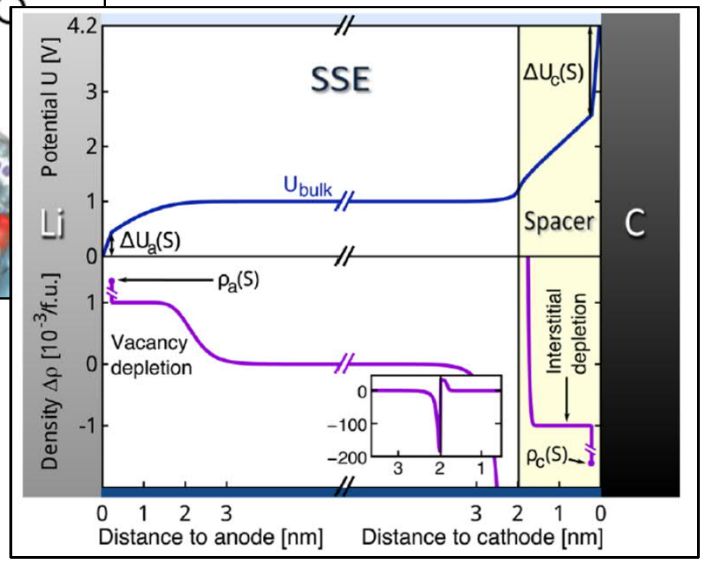


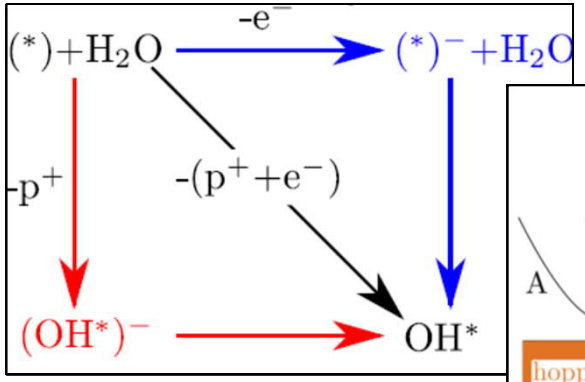
Working interfaces



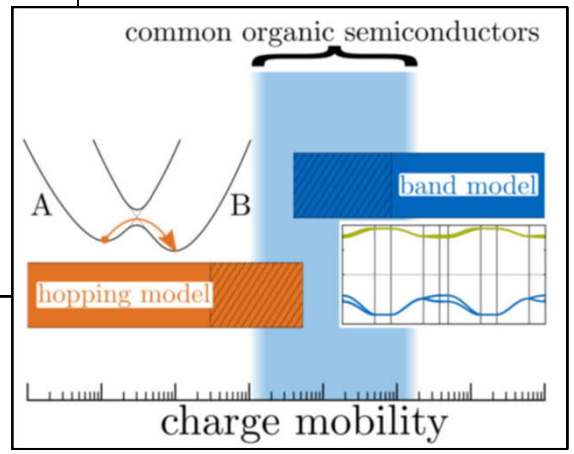


Environmental effects

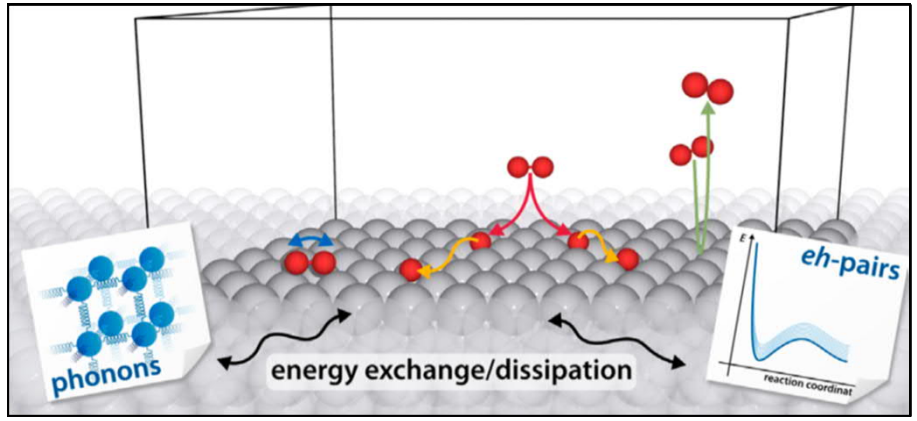




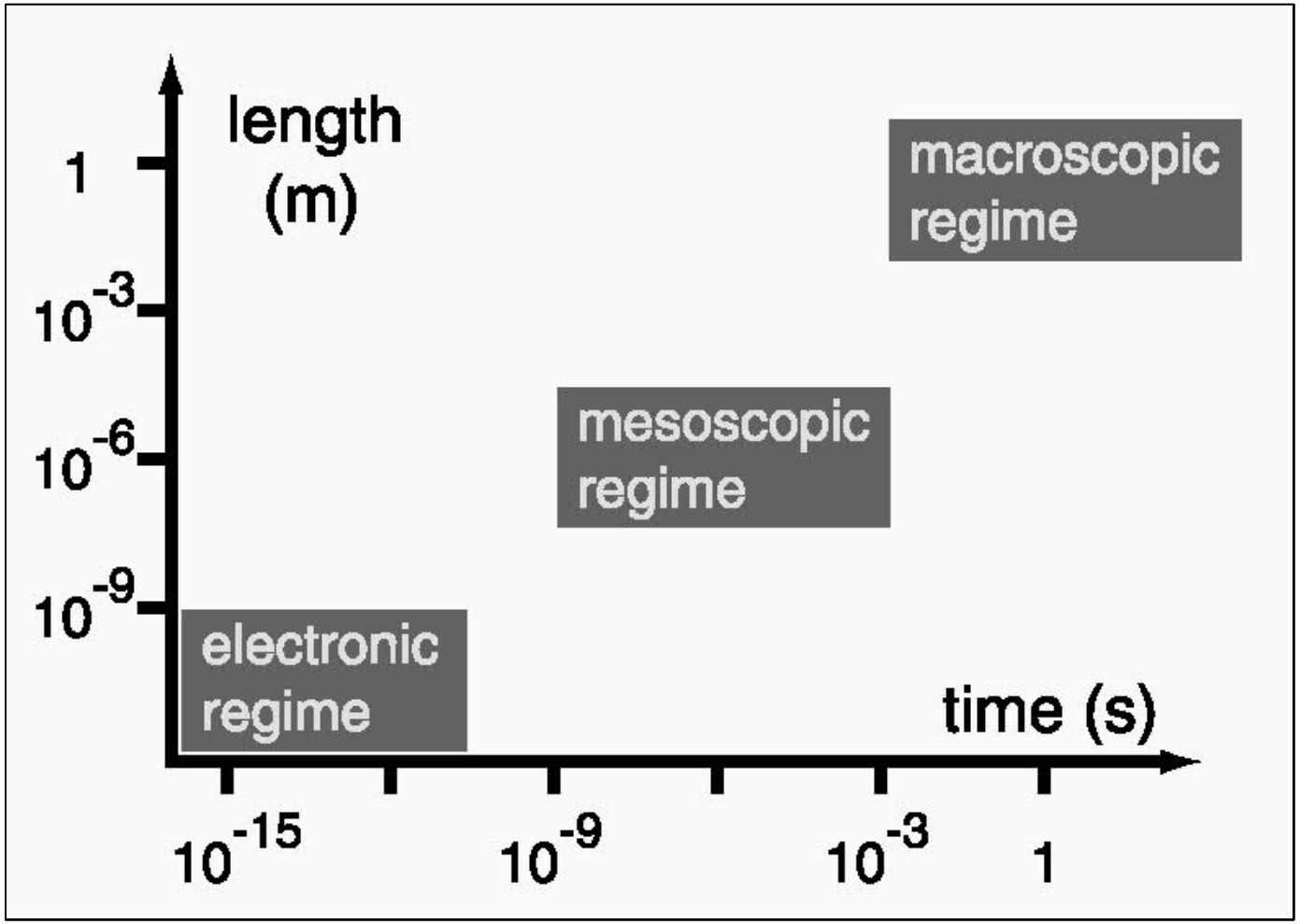
Mechanisms



Degree of adiabaticity



Multiphysics – Multiscale Modeling

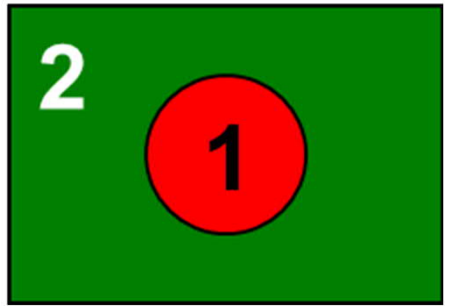


General Concepts

Linking approaches

concurrent (embedding)

sequential/hierarchical (hand-shaking)



Coarse-graining

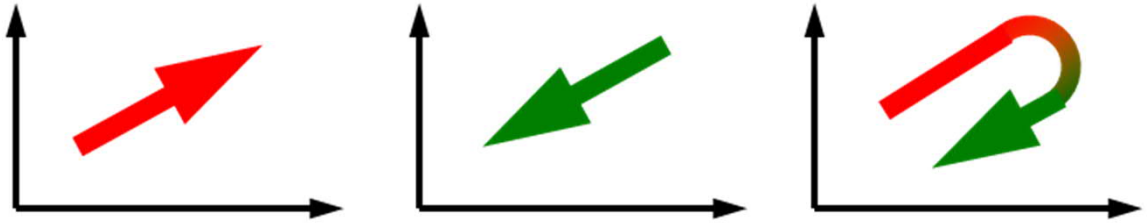
information overflow

typical: electronic → molecular → pseudo-particle/lattice → continuum

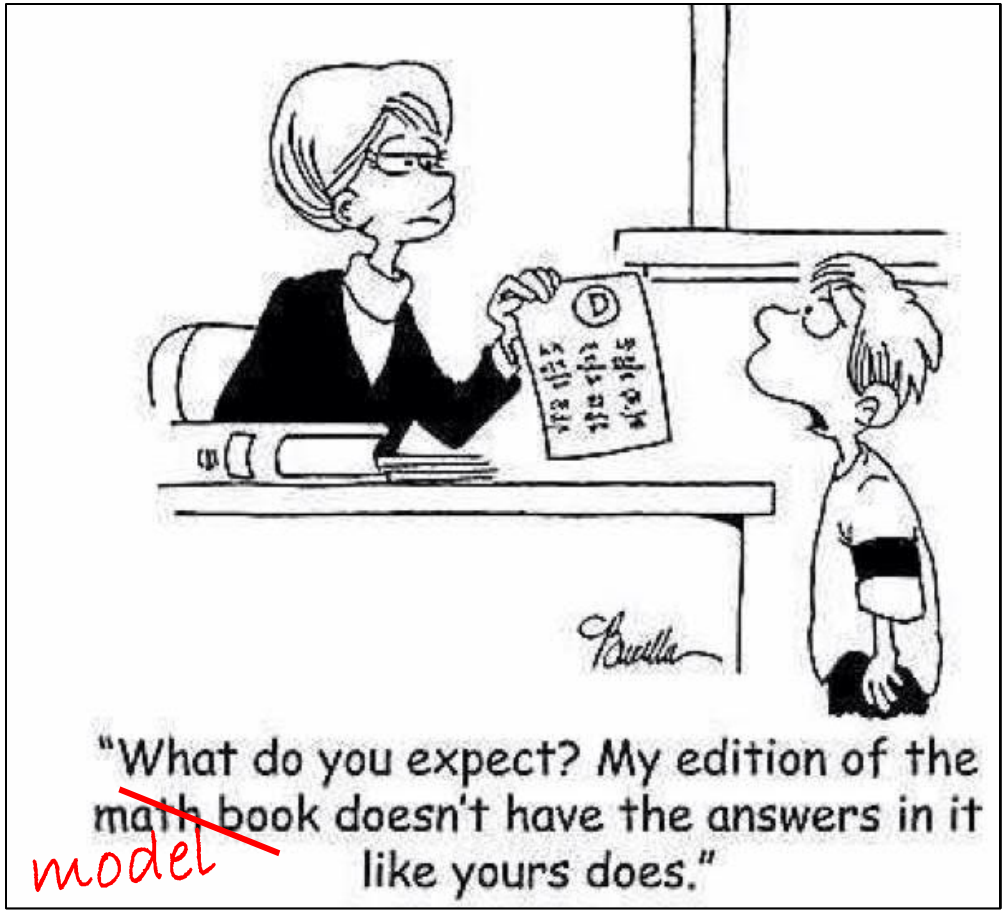
Reverse-mapping capability

bottom-up vs. top-down

predictive-quality vs. empirical modeling



Phenomenological vs. Predictive Theory



“Predictive Power”: First-Principles Electronic Structure Theory

Potential energy for fixed nuclear positions $\{\mathbf{R}_I\}$:

$$E_0(\{\mathbf{R}_I\}) = \mathrm{Min}_\Psi \langle\Psi| H^e\{\mathbf{R}_I\} |\Psi\rangle$$

1. Wavefunction based methods („Quantum Chemistry“)

Ansatz for Ψ: Hartree-Fock, post-HF (MP2, CI, CC,…)

2. Density-functional theory $\Psi = \Psi[n(\mathbf{r})]$ (Hohenberg-Kohn, 1964)

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

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

(Kohn-Sham, 1965)

$$E^{XC}_{LDA}[n] = \int d^3r\, n(r)\, \varepsilon^{XC}(n_o)\Big|_{n_o=n(r)}$$

$$E^{XC}_{GGA}[n] = \int d^3r\, n(r) \varepsilon^{XC}(n_o, \nabla n_o)\Big|_{n_o=n(r)}$$

Ab initio Thermodynamics: General Approach

Motivation (Scheffler, ~1980s):

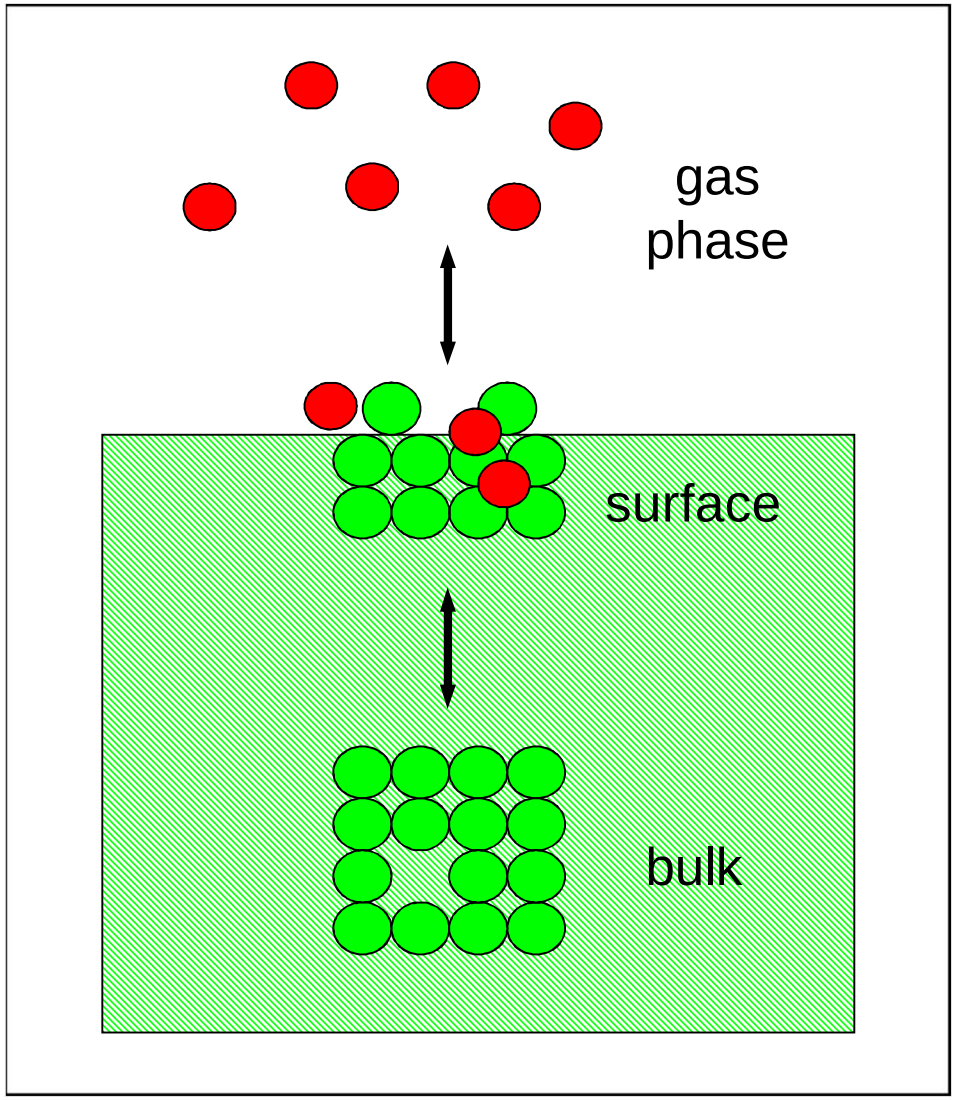
- extend length scale
- consider finite temperature effects

Approach:

- separate system into sub-systems (exploit idea of infinite (homogeneous) reservoirs!)
- calculate properties of sub-systems separately (cheaper…)
- connect by implying equilibrium between sub-systems

Drawback:

- no temporal information („system properties after infinite time“)
- equilibrium assumption



J. Rogal and K. Reuter, *Ab initio atomistic thermodynamics for surfaces: A primer*. In: Experiment, Modeling and Simulation of Gas-Surface Interactions for Reactive Flows in Hypersonic Flights. Educational Notes RTO-EN-AVT-142, Neuilly-sur-Seine (2007).

II. Recap:

Essential thermodynamics and statistical mechanics

Thermodynamics in a Nutshell

Internal energy (U)	$E(S,V)$	
Enthalpy	$H(S,p)$	$= E + pV$
(Helmholtz) free energy	$F(T,V)$	$= E - TS$
Gibbs free energy	$G(T,p)$	$= E - TS + pV$

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: $dE^{tot} = dQ + dW$, $dW = -pdV$, $dQ = TdS$)

$$dE = TdS - pdV$$
$$dH = TdS + Vdp$$
$$dF = -SdT - pdV$$
$$dG = -SdT + Vdp$$

$\Rightarrow$ These expressions open the gate to a whole set of general relations like:

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

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

$(\partial T/\partial V)_S = -(\partial p/\partial S)_V$ 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 system states

$\Rightarrow F = - k_B T \ln(Z)$

- 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

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

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

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

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

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

Required input: Internal energy E (molecule vs. mole! ZPE!)

Ground state spin degeneracy I_{spin}

<u>ii) Transl. free energy</u> $\quad Z_{trans} = \sum_{\underline{k}} \exp(-\hbar k^2 / 2mk_B T)$ Particle in a box of length $L = V^{1/3}$

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

Required input: Particle mass m

Computation of Free Energies: Ideal Gas (cont'd)

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

(Diatomic molecule) $\Rightarrow$ $Z_{rot} \approx -k_B T \ \ln(k_B T/\sigma B_o)$

$\sigma = 2$ (homonucl.), $= 1$ (heteronucl.)

$B_o \sim md^2$ (d = bond length)

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

<u>iv) Vibrational free energy</u> $Z_{vib} = \sum_{i=1}^{M} \sum_n \exp(-(n + ½)\hbar\omega_i / k_B T)$ Harmonic oscillator

$$\Rightarrow \mu_{vib}(T) = \sum_{i=1}^{M} ½ \hbar\omega_i + k_B T \ln(1 - \exp(-\hbar\omega_i/k_B T))$$

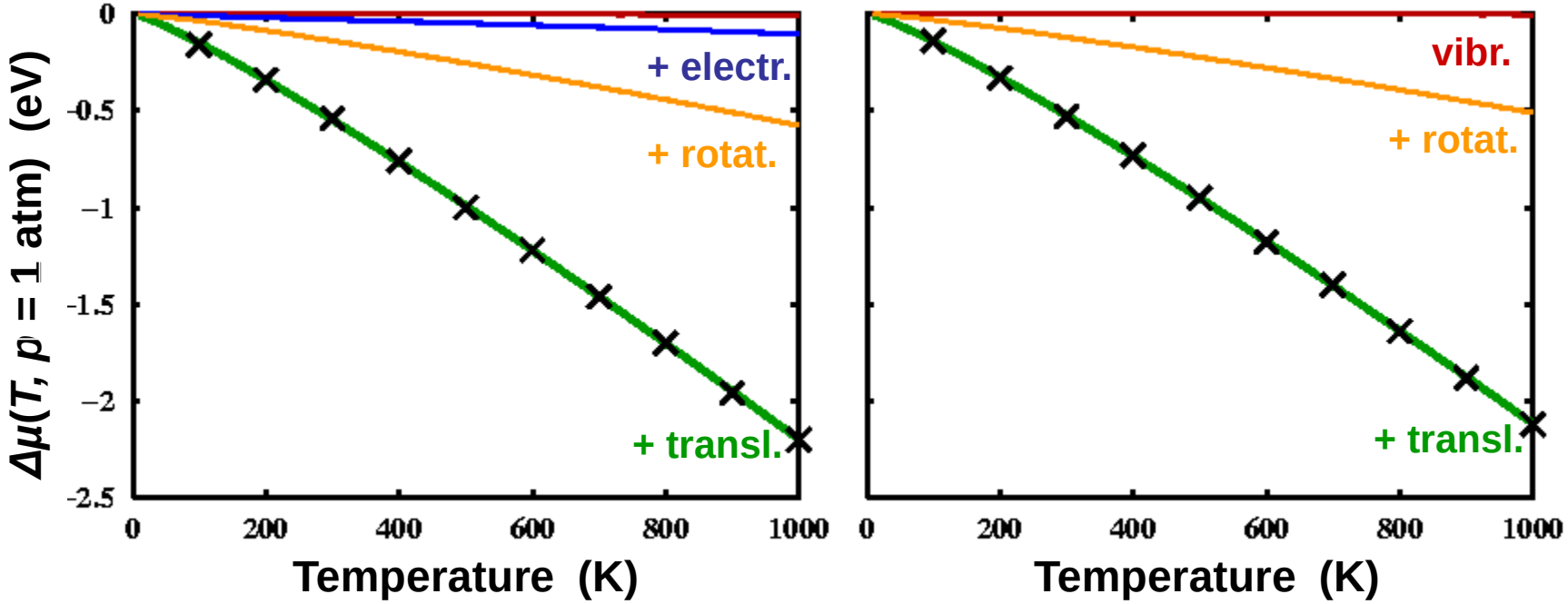
Required input: M fundamental vibr. modes ω_i

Calculate dynamic matrix $D_{ij} = (m_i m_j)^{-½} (\partial^2 E/\partial r_i \partial r_j)_{\underline{r}_{eq}}$
Solve eigenvalue problem $\det(D - 1\ \omega_i^2)$

Computation of Free Energies: Ideal Gas (cont'd)

		O_2	CO
m	(amu)	32	28
$\nu_{stretch}$	(meV)	196	269
B_o	(meV)	0.18	0.24
σ		2	1
I_{spin}		3	1

$$\mu = \mu(T,p) = E + \Delta\mu(T,p)$$



Alternatively: $\Delta\mu(T, p) = \Delta\mu(T, p^o) + kT \ln(p/p^o)$
and $\Delta\mu(T, p^o = 1\text{ atm})$ tabulated in thermochem. tables (e.g. JANAF)

Computation of Free Energies: Solids

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

F^{trans}	Translational free energy	$\propto 1/M \rightarrow 0$
F^{rot}	Rotational free energy	
pV	$V = V(T,p)$ from equation of state, varies little	$\rightarrow 0$ for $p < 100$ atm
F^{conf}	Configurational free energy	$\rightarrow$ Trouble maker…
E	Internal energy	$\rightarrow$ DFT (periodic supercell!)
F^{vib}	Vibrational free energy	$\rightarrow$ phonon band structure

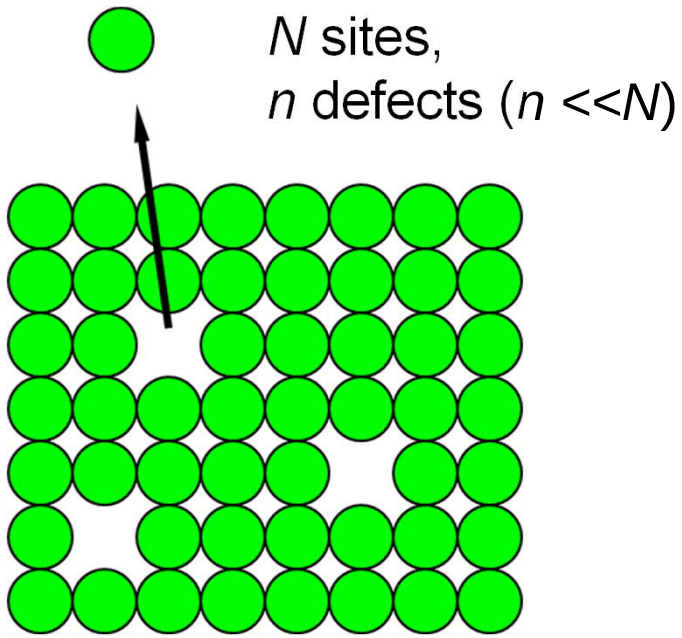
E, F^{vib} use differences
use simple models to approx. F^{vib} (Debye, Einstein)

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

Toy Example: Concentration of Point Defects

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: $E = n\,E_D$

Config. entropy: $F^{conf} = k_B T \ln Z(n)$

with $$Z = \frac{N\,(N-1)\,\ldots\,(N-n-1)}{1\cdot 2\cdot\,\ldots\cdot\,n} = \frac{N!}{(N-n)!\,n!}$$

Minimize free energy: $$(\partial G/\partial n)_{T,p} = \partial/\partial n_{T,p}\,(E - F^{conf} + pV) = 0$$

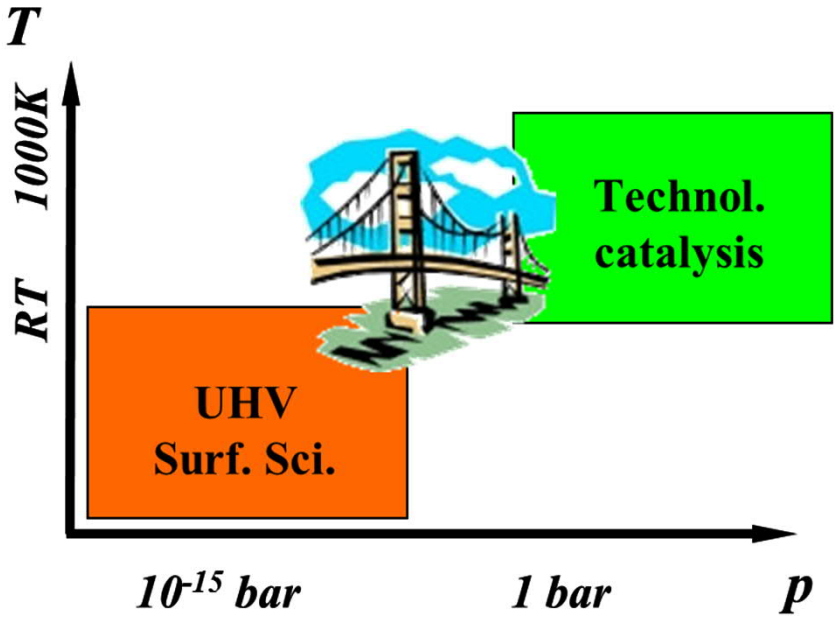
Forget pV, use Stirling: $\ln N! \approx N(\ln N - 1)$ $\Rightarrow$ $$\boxed{n/N = \exp(-E_D/k_B T)}$$

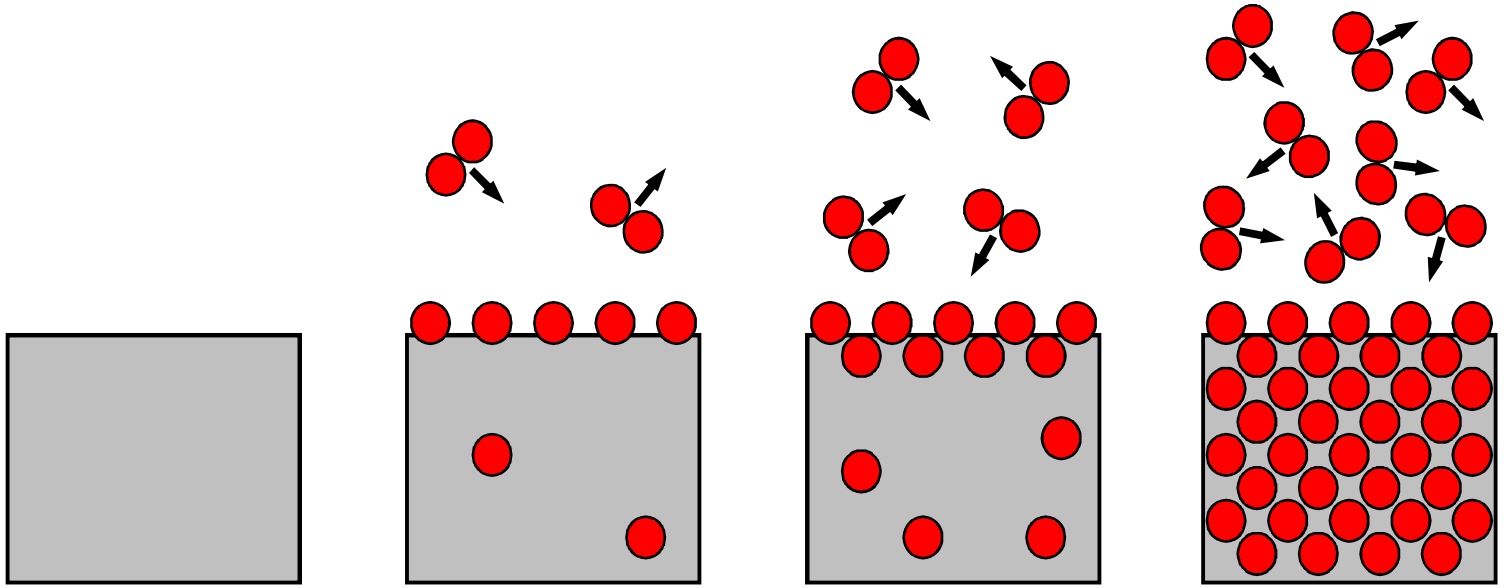
Solid State Physics, N.W. Ashcroft and N.D. Mermin, Holt-Saunders (1976)

III. Towards Surfaces:

Ab initio thermodynamics for oxide formation

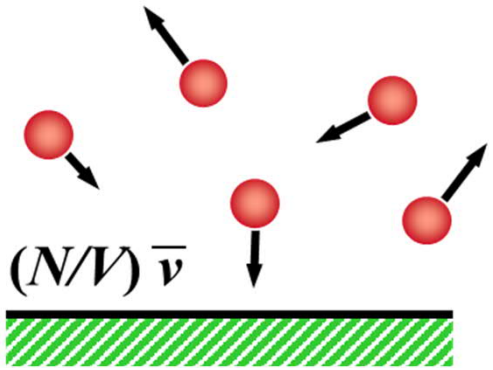
Oxidation Catalysis and the Pressure Gap: Metal, Oxide, Both, … ?!





Nanometer and sub-nanometer thin oxide films at surfaces of late transition metals, K. Reuter, in “Nanocatalysis”, U. Heiz, U. Landman (Eds.), Springer, Berlin (2006). ISBN 978-3-540-32645-8.

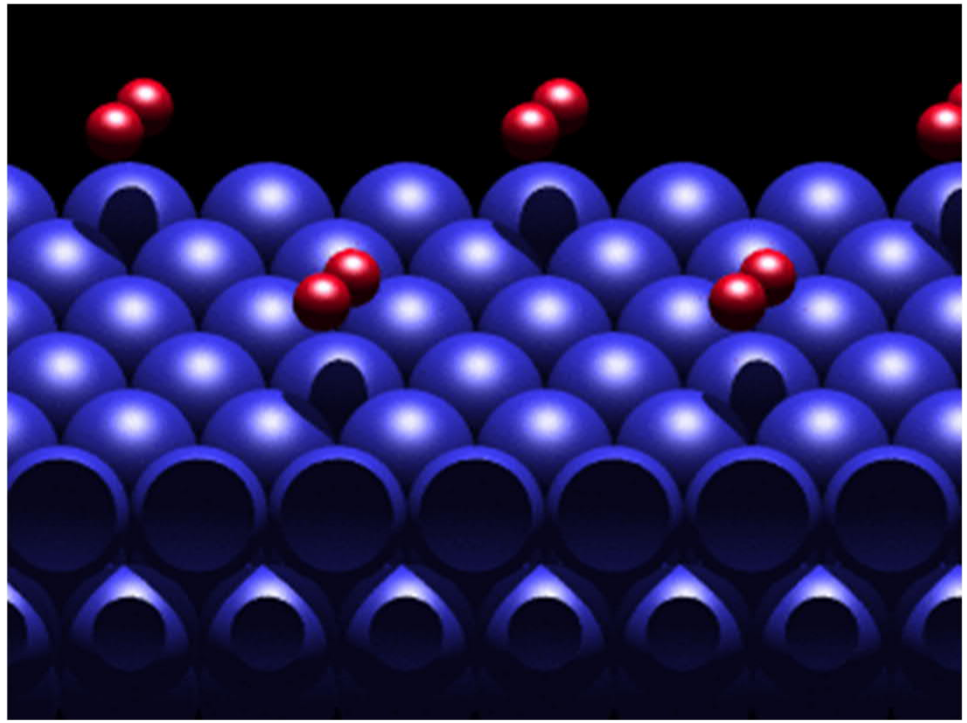
Keeping Everything: Expensive, Limited Time Scale



$$Z = \frac{p}{(2\pi mkT)^{1/2}}$$

10^{15} sites/cm^2, T = 300 K,

p = 1 atm: $Z \sim 10^8$ site^{-1} s^{-1} !!



Example:

O_2 dissociation at Al(111)

Total time of trajectory: 0.5 ps
Time step: 2.5 fs (200 steps)

CPU cost: 45 days on 1 Compaq (2005) ES45 processor

J. Behler *et al.*, Phys. Rev. Lett. 94, 036104 (2005)

Ab initio Thermodynamics: General Approach

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Approach:

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Drawback:

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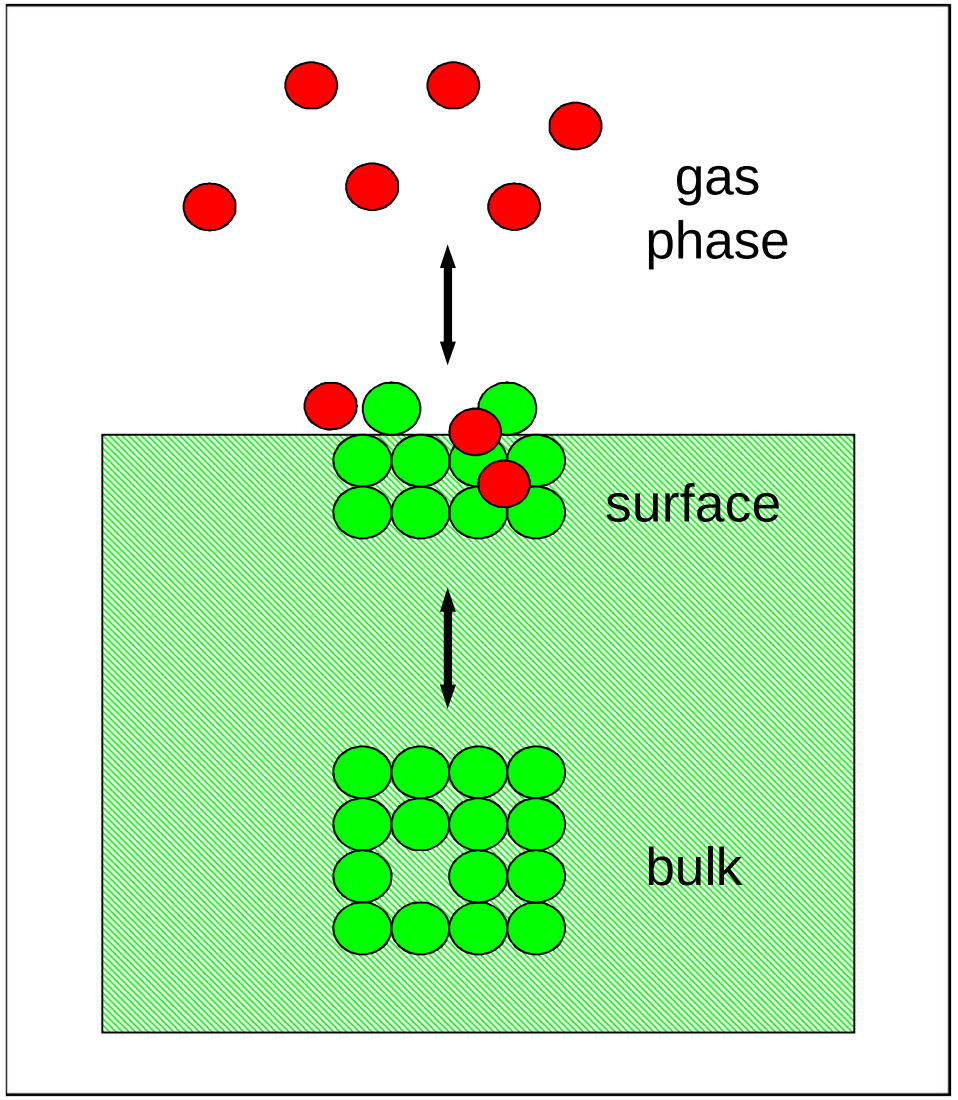

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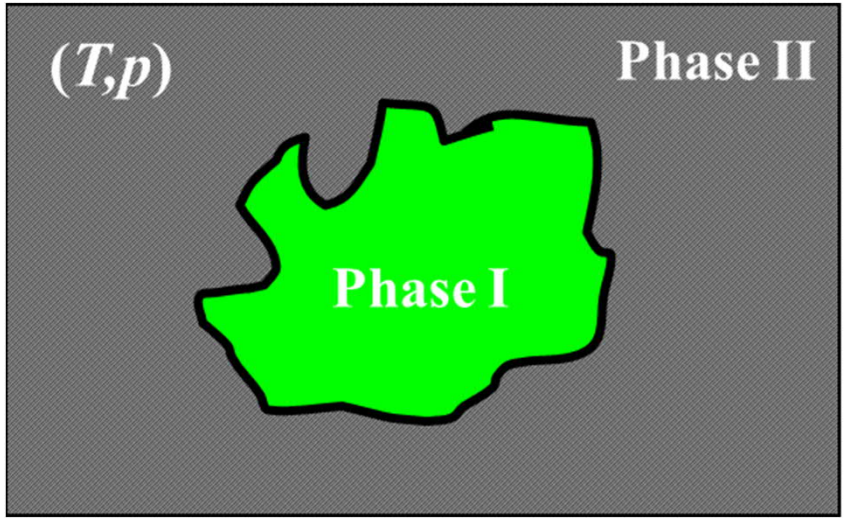
Surface Thermodynamics

A surface can never be alone:
there are always
"two sides" to it !!!



solid – gas
solid – liquid
solid – solid ("interface")
…

Phase I / phase II alone (bulk):

$$G_I = N_I\, \mu_I$$
$$G_{II} = N_{II}\, \mu_{II}$$

Total system (with surface):

$$G_{I+II} = G_I + G_{II} + \Delta G_{surf}$$

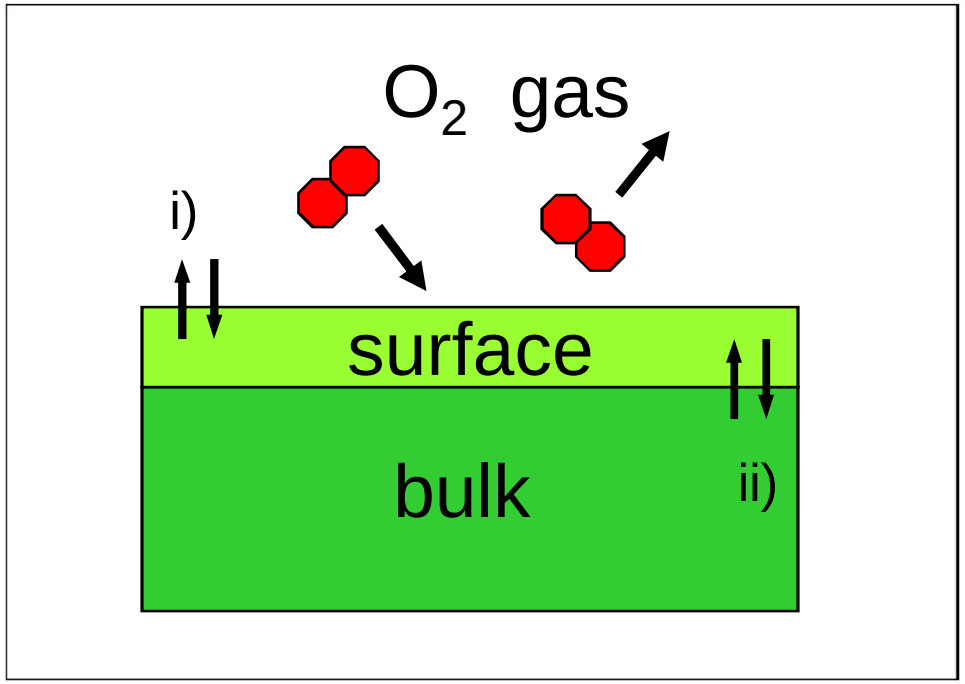
γA

$$\gamma = 1/A \left(G_{I+II} - \sum_i N_i\, \mu_i \right)$$

Surface tension
(free energy per area)

Surface in Contact with an Oxygen Gas Phase

$$\gamma_{\text{surf.}} = 1/A \left[G_{\text{surf.}}(N_O, N_M) - N_O \ \mu_O - N_M \mu_M \right]$$



Use reservoirs:

i) μ_O from ideal gas

ii) $\mu_M = g_M^{\text{bulk}}$

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

Forget about F^{vib} and F^{conf} for the moment, pV is negligible:

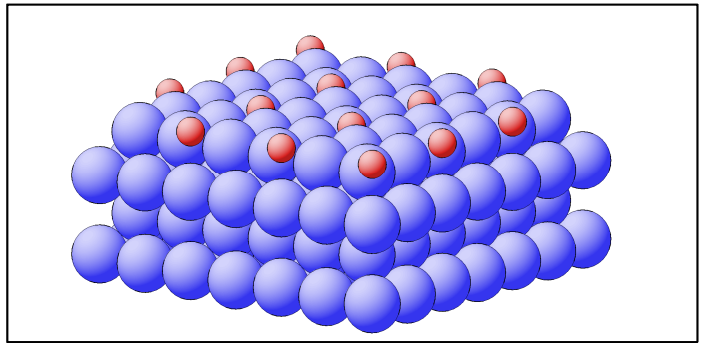
$$\gamma(T,p) \approx \left(E_{\text{surf.}}^{(\text{slab})} - N_M E_M^{\text{bulk}} \right)/A - N_O \mu_O(T,p)/A$$

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

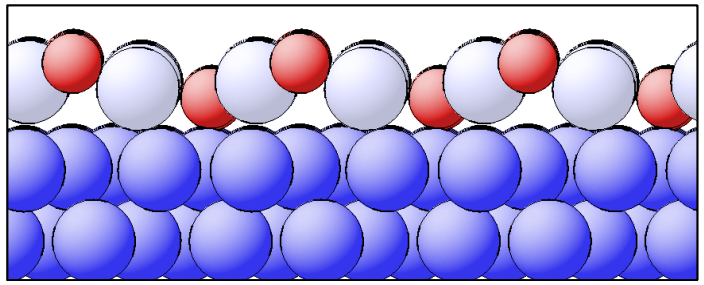
Oxide Formation on Pd(100)

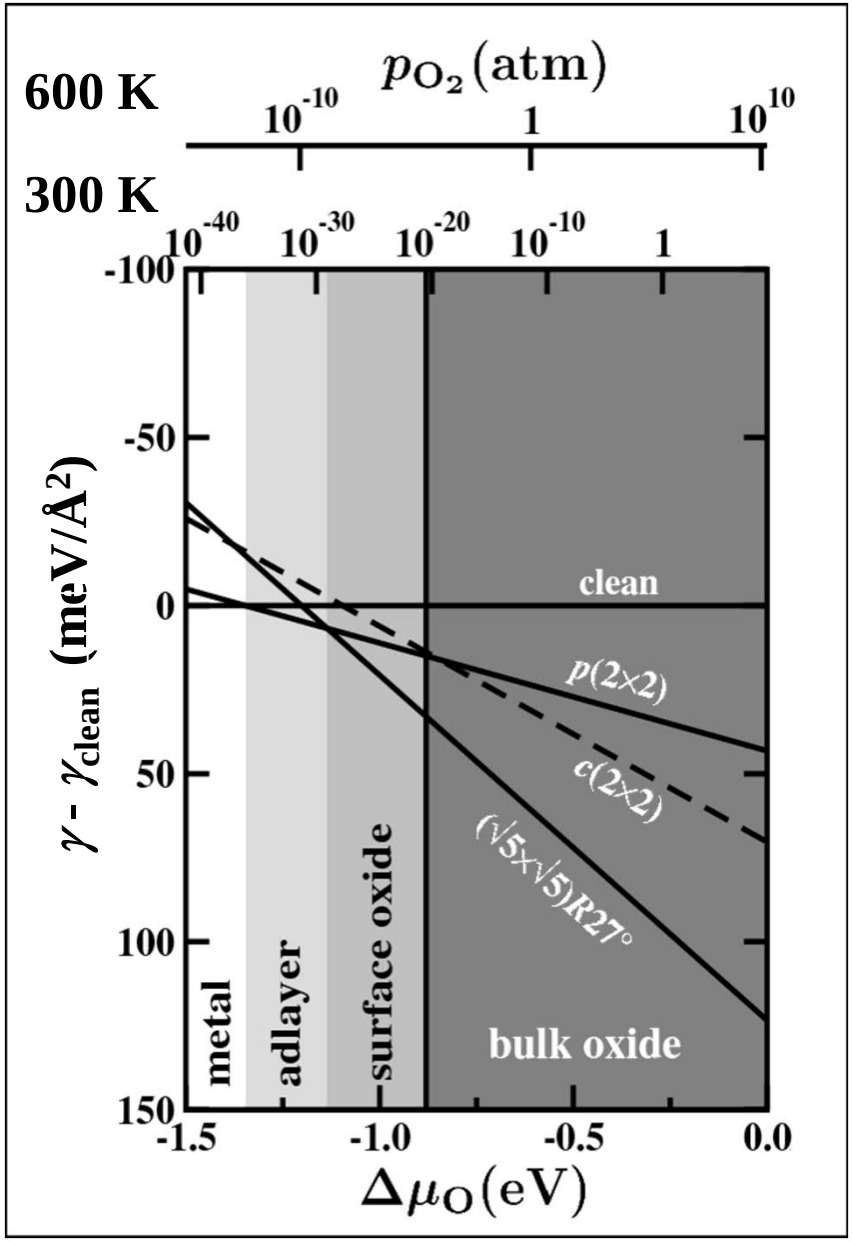
$$\gamma \approx \left(E_{\text{surf.}}^{(\text{slab})} - N_M E_M^{\text{bulk}} \right)/A - N_O \mu_O/A$$

p(2x2) O/Pd(100)



(√5 x √5)R27° PdO(101)/Pd(100)





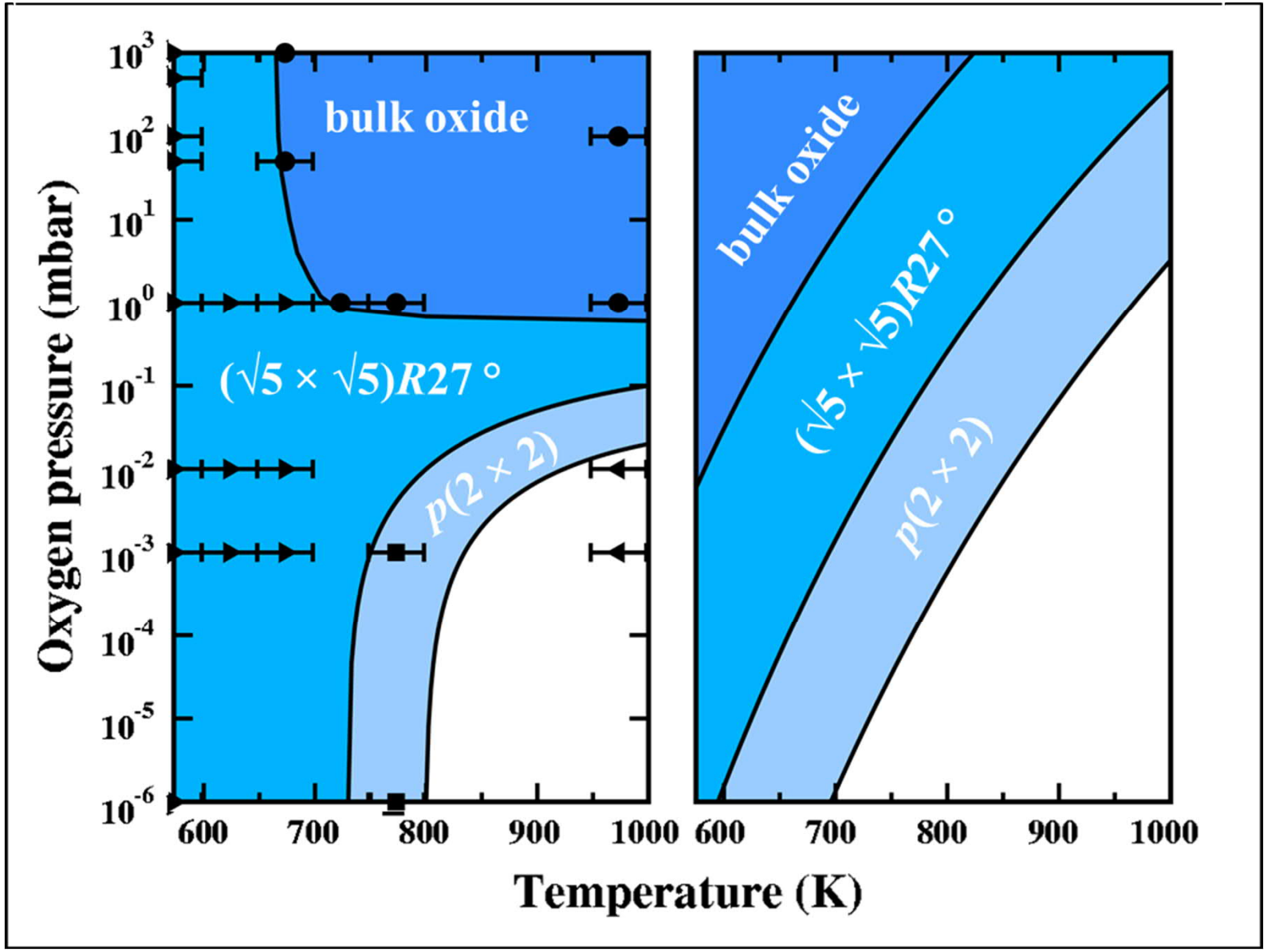
K. Reuter and M. Scheffler
Appl. Phys. A 78, 793 (2004)

Comparing with Experiment: Kinetic Effects

Experiment:
E. Lundgren (U Lund)
A. Stierle (MPG Stuttgart)

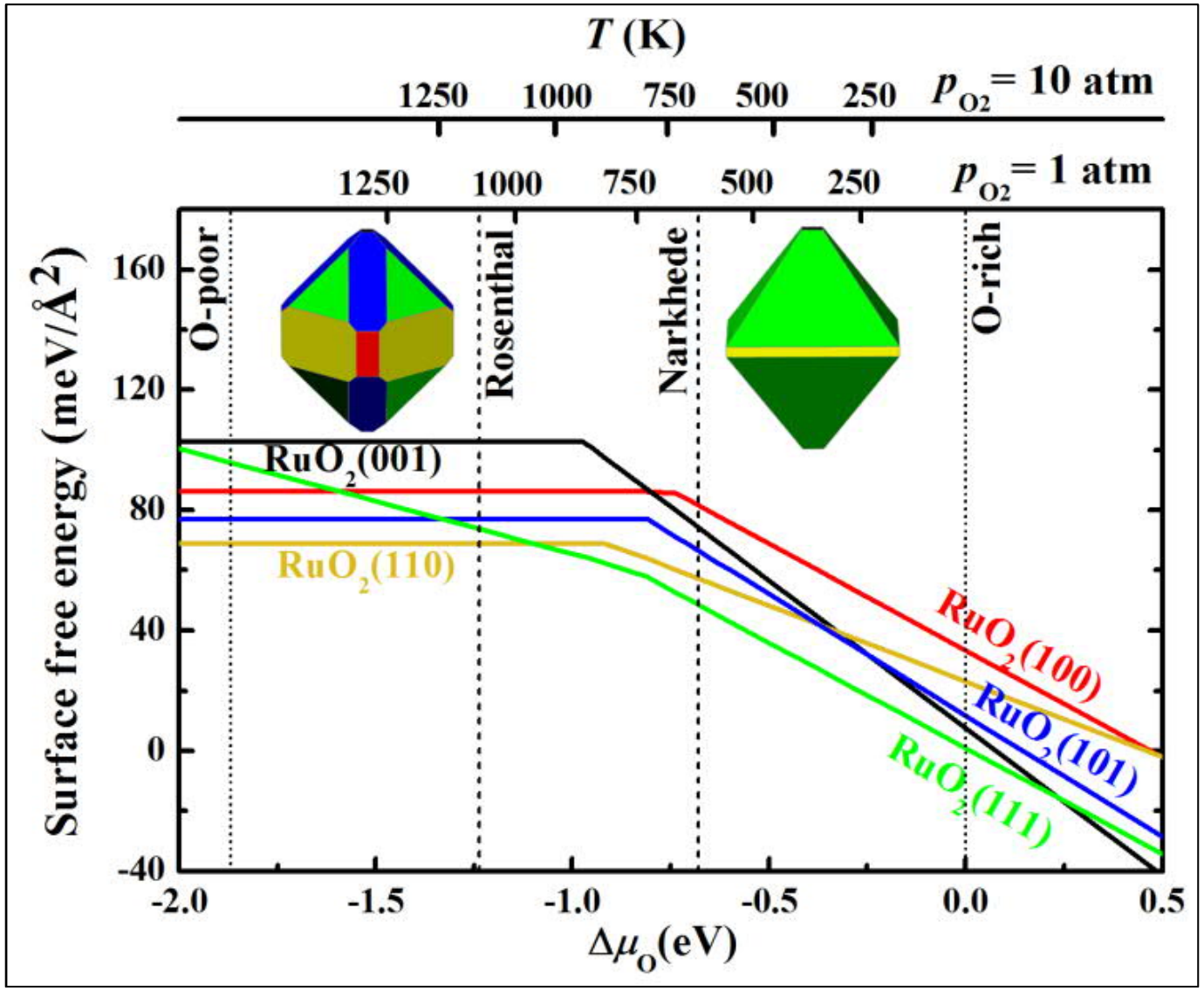
Heterogeneous Catalysis
$\mu = \mu(T,p_i)$: Phase diagrams

Electrocatalysis
$\mu = \mu(U,\text{pH})$: Pourbaix diagrams

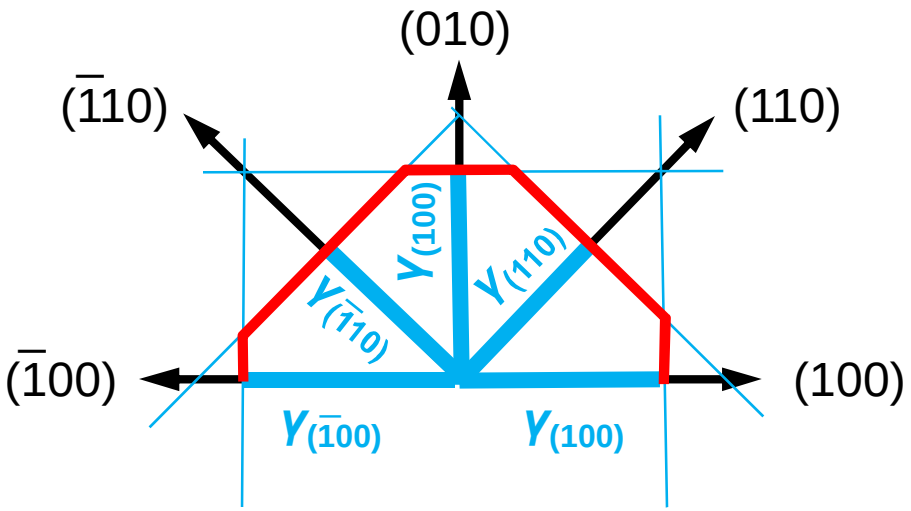


E. Lundgren *et al.*,
Phys. Rev. Lett. 92, 046101 (2004)

Particle Shapes: Wulff Constructions



Equilibrium shape will minimize $\int dA\ \gamma$



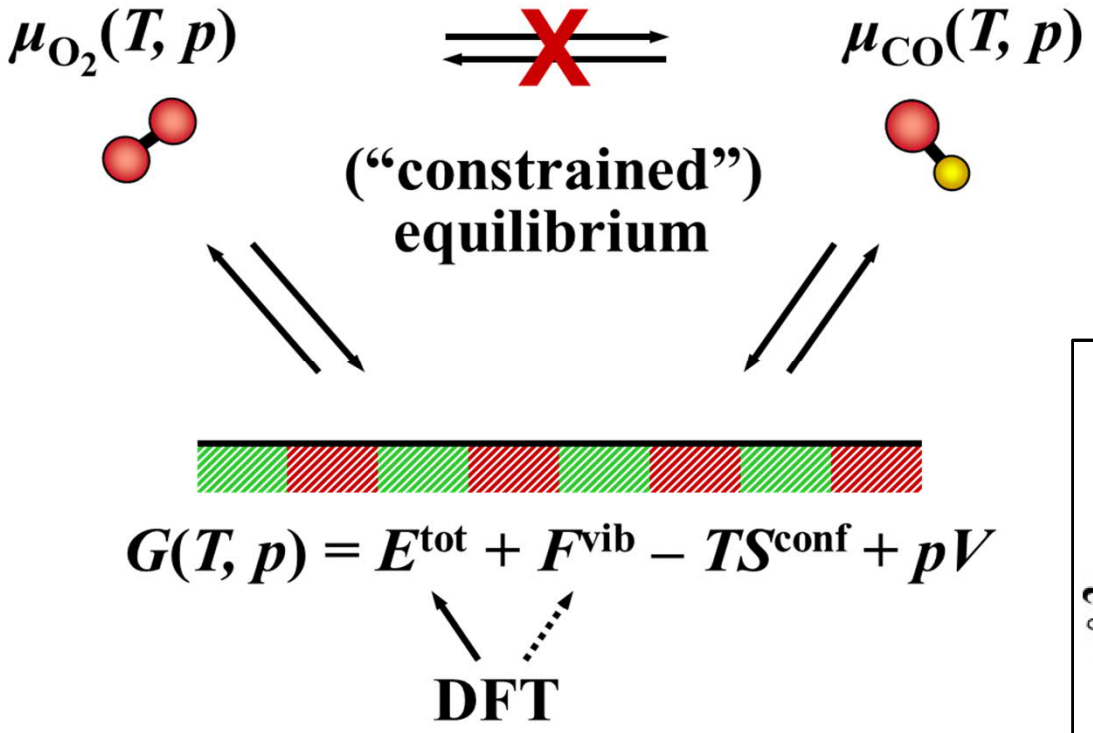
Wulff construction:
Shape of free nanoparticle

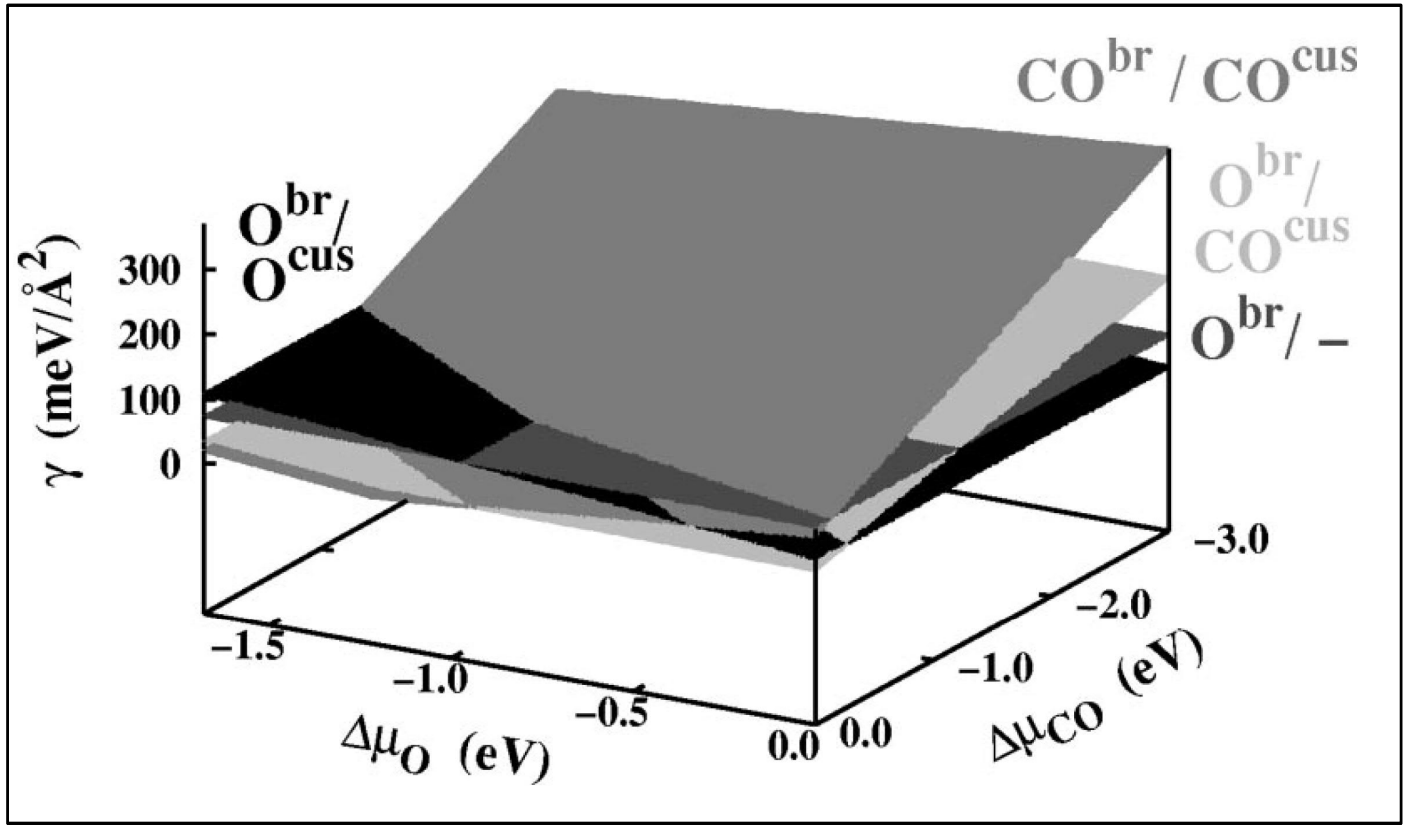
Wulff-Kaichew construction:
Shape of supported nanoparticle
(contact angle)

T. Wang, J. Jelic, D. Rosenthal, and K. Reuter, Chem. Cat. Chem. 5, 3398 (2013)

IV. *Ab initio* Thermodynamics goes Catalysis: „Constrained“ equilibria and configurational entropy

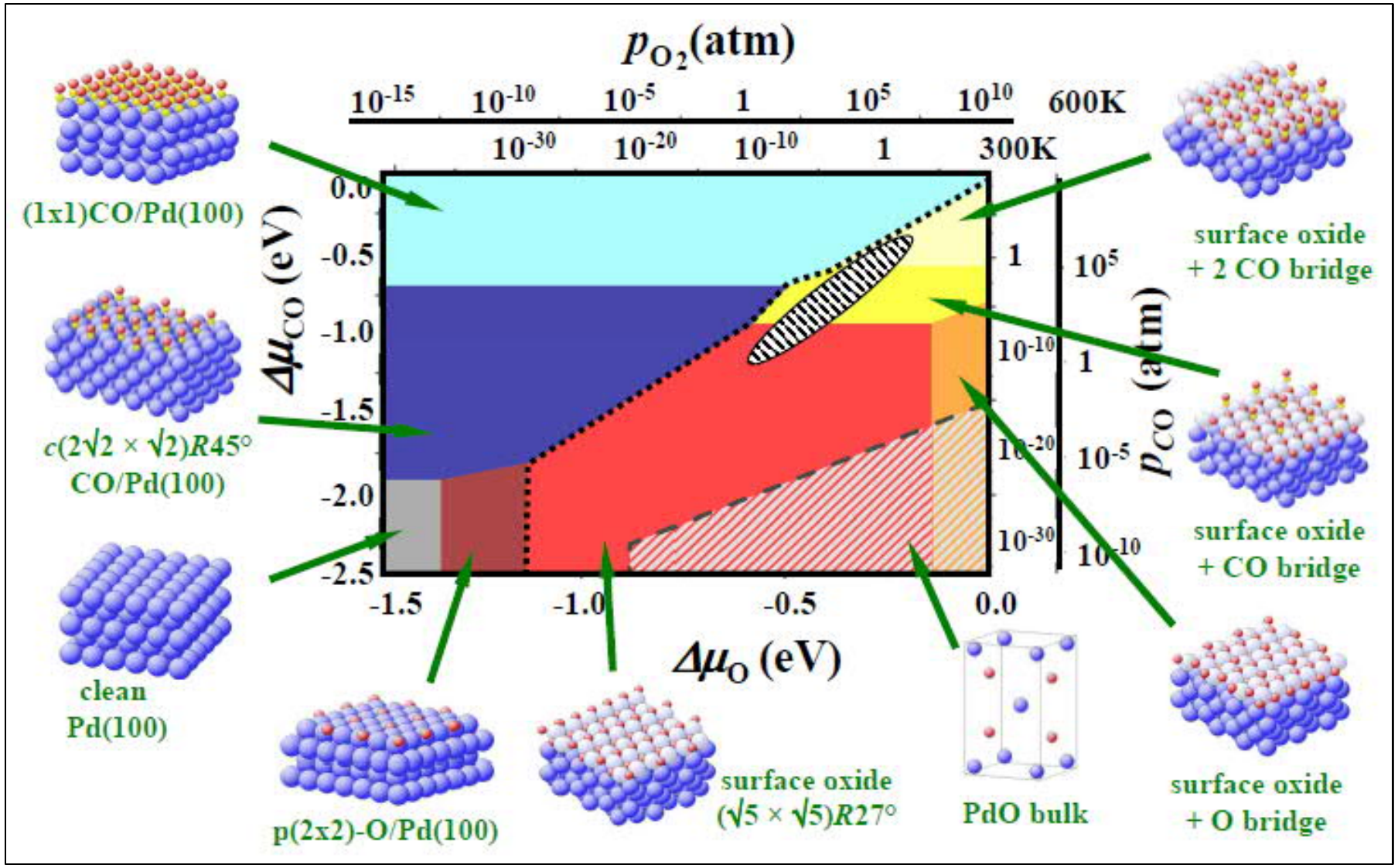
So, Catalysis is all about Kinetics, isn't it?





K. Reuter and M. Scheffler,
Phys. Rev. B 68, 045407 (2003);
Phys. Rev. Lett. 90, 046103 (2003)

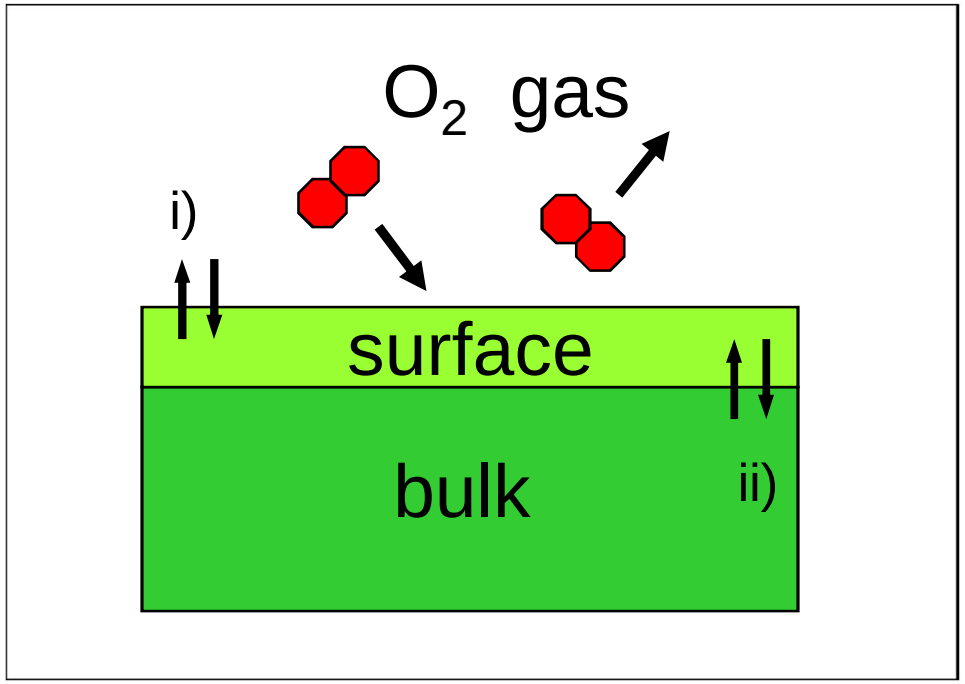
Surface Oxide Formation in CO Oxidation at Pd(100)



J. Rogal, K. Reuter, and M. Scheffler, Phys. Rev. Lett. 98, 046101 (2007)

Remember: Surface in Contact with an Oxygen Gas Phase

$$\gamma_{\text{surf.}} = 1/A \left[G_{\text{surf.}}(N_O, N_M) - N_O \ \mu_O - N_M \mu_M \right]$$



Use reservoirs:

i) μ_O from ideal gas

ii) $\mu_M = g_M^{\text{bulk}}$

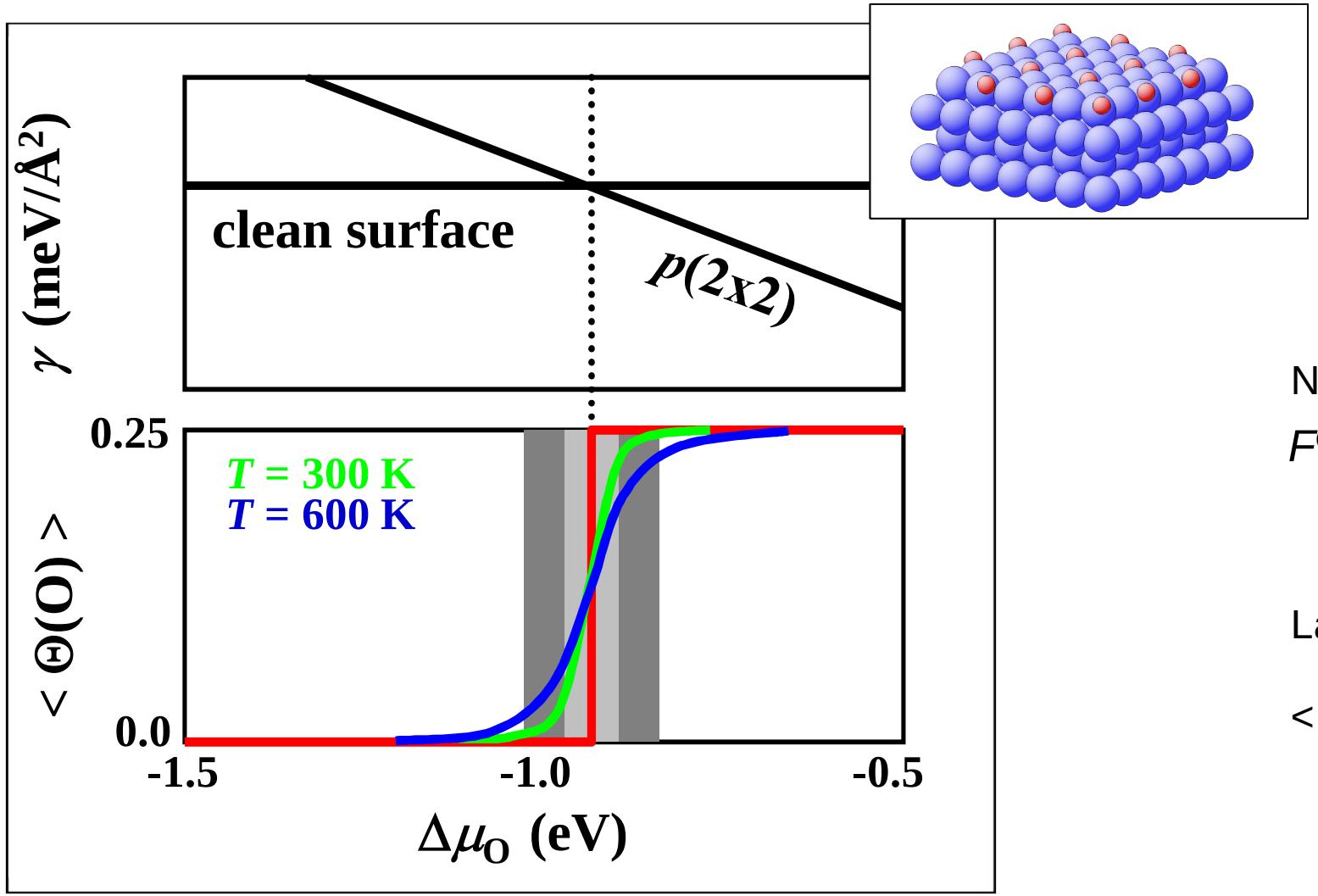
$$G(T, p) = E + F^{\text{vib}} + F^{\text{conf}} + pV$$

Forget about F^{vib} and F^{conf} for the moment, pV is negligible:

$$\gamma(T,p) \approx \left(E_{\text{surf.}}^{(\text{slab})} - N_M E_M^{\text{bulk}} \right)/A - N_O \mu_O(T,p)/A$$

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

Configurational Entropy and Phase Transitions



No lateral interactions:

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

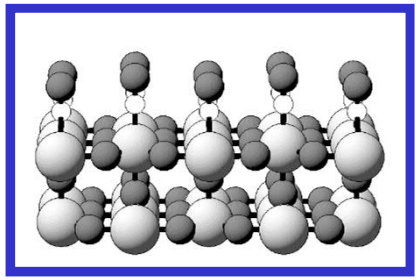
Langmuir adsorption-isotherm

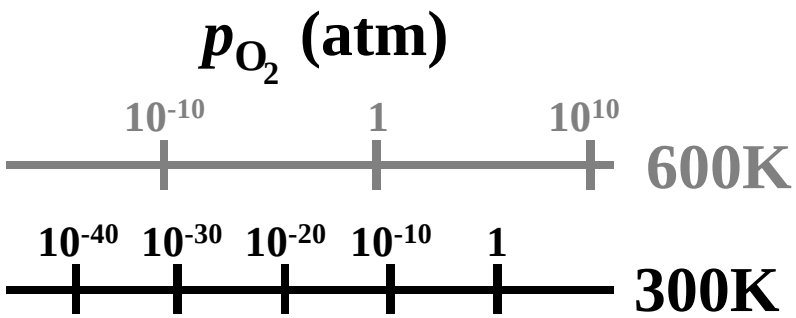
$$< \theta(O^{cus}) > = \frac{1}{1 + \exp\left((E^{ad} - \Delta\mu_O)/k_B T\right)}$$

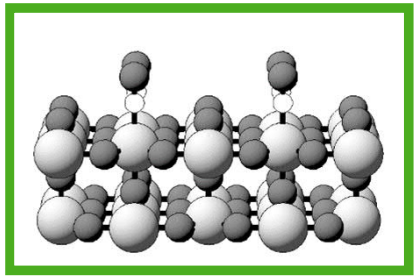
Configurational entropy smears out phase transitions

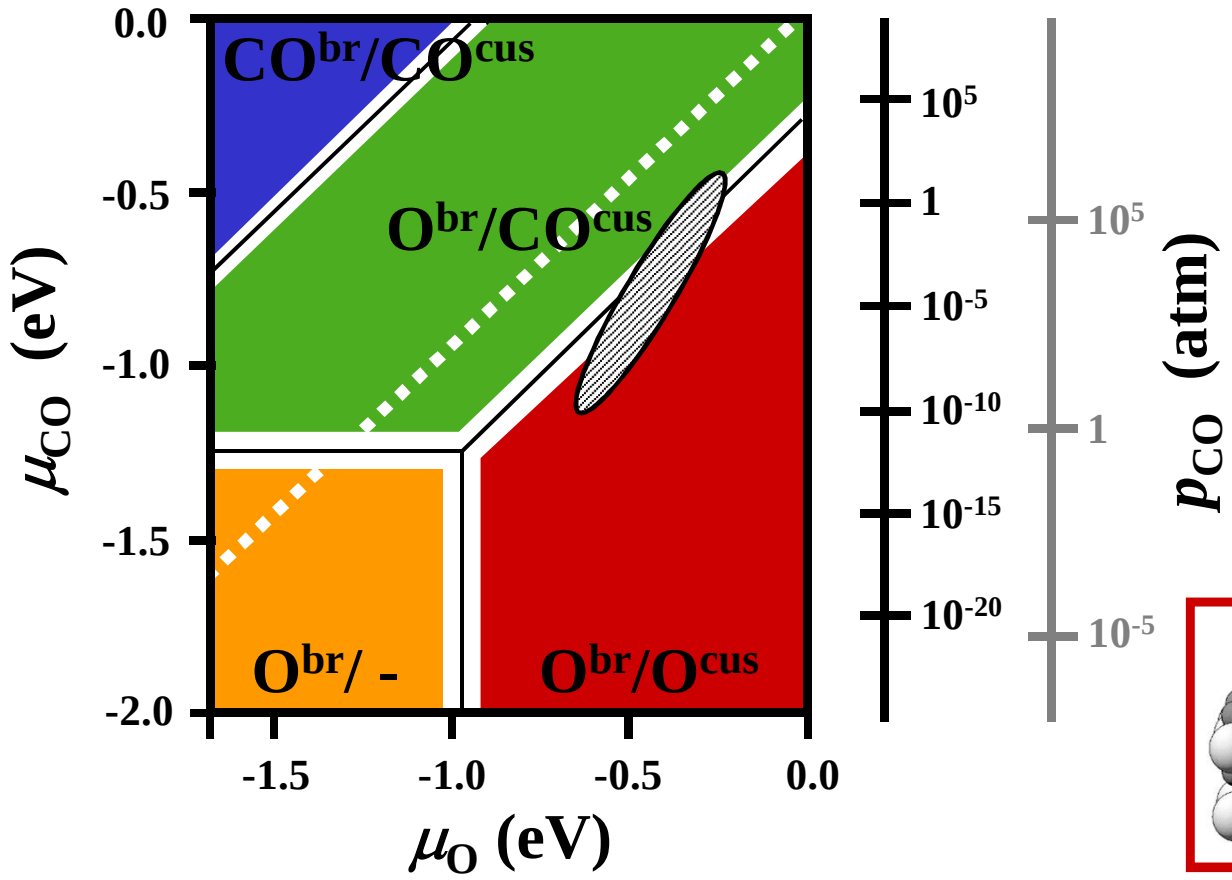
Catalysis as a Phase Transition Phenomenon

K. Reuter and M. Scheffler,
Phys. Rev. B 68, 045407 (2003);
Phys. Rev. Lett. 90, 046103 (2003)

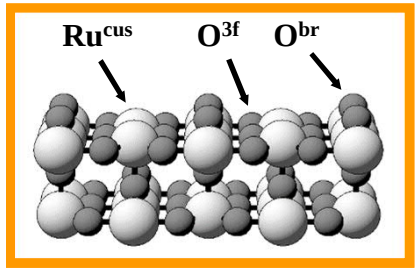


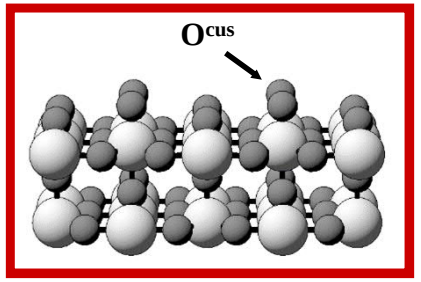






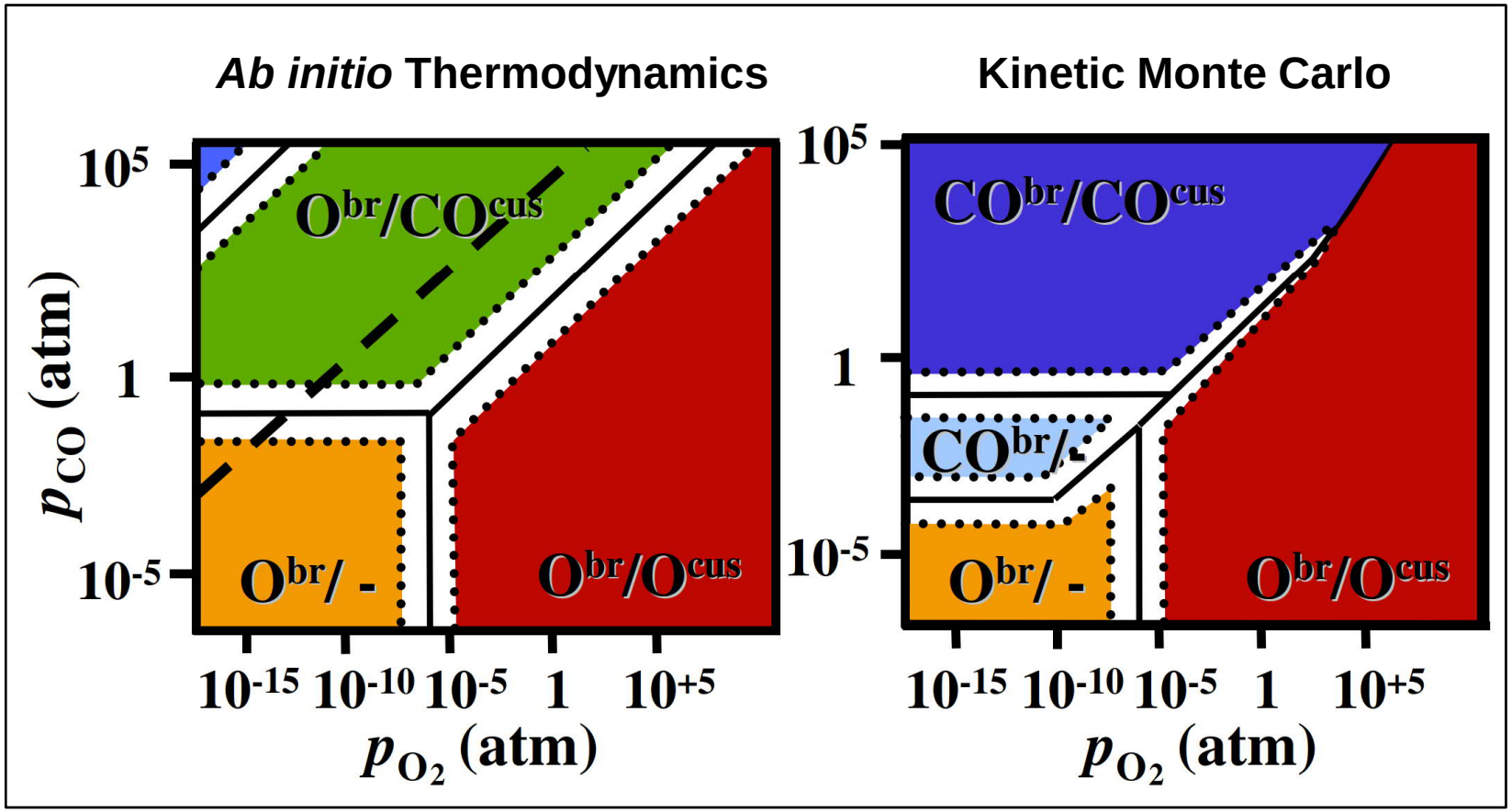
CO Oxidation
at RuO_2(110)





Beware: Kinetic Effects

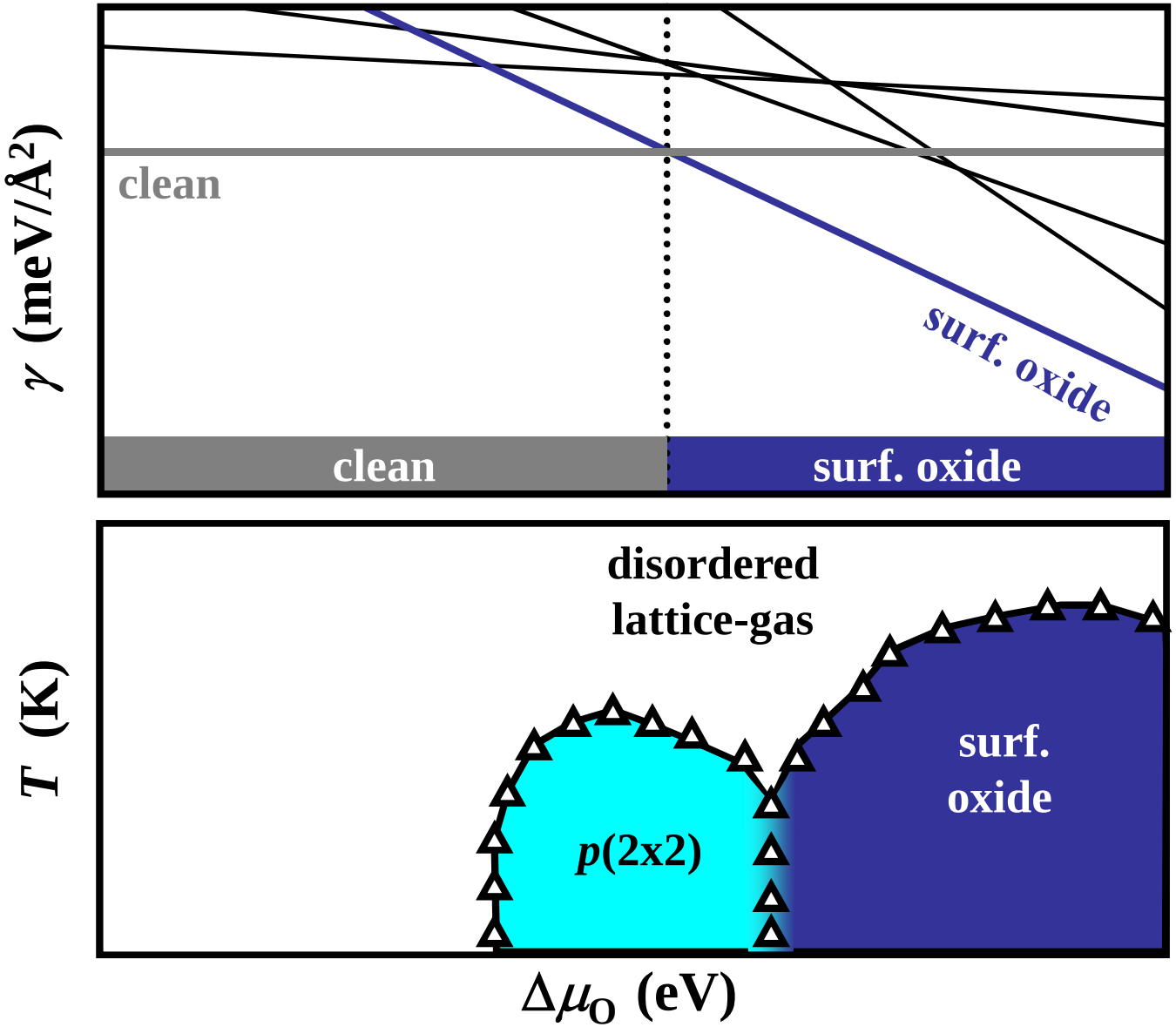
CO Oxidation at $RuO_2(110)$



Reaction consumes O^{br} population faster than can be replenished from the gas phase

K. Reuter, in "Modelling and Simulation of Heterogeneous Catalytic Reactions: From the Molecular Process to the Technical System", O. Deutschmann (Ed.), Wiley-VCH, Weinheim (2011)

Beware: Configurational Sampling and Configurational Entropy



Any *ab initio* thermodynamics phase diagram is only as good as the structures that were sampled!

Ab initio Thermodynamics: General Approach

Motivation (Scheffler, ~1980s):

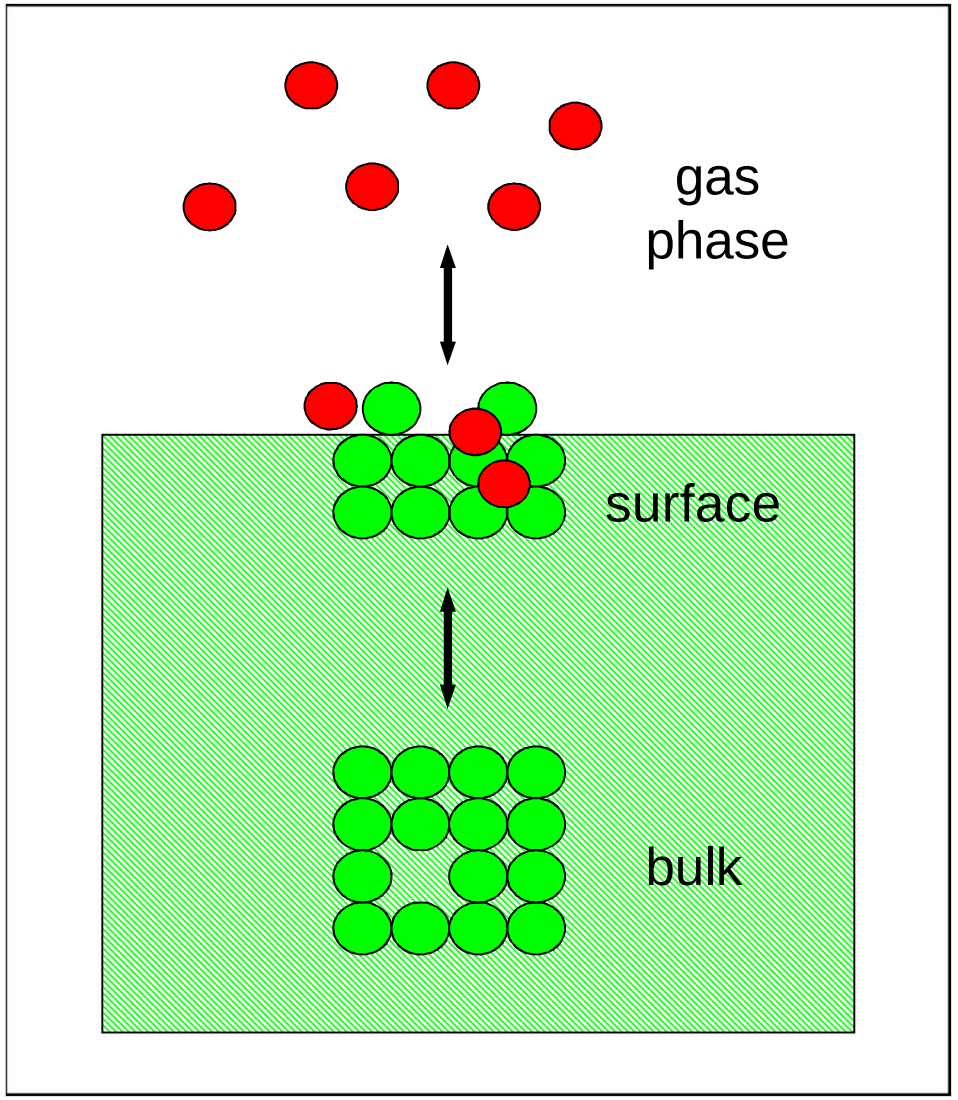
- extend length scale
- consider finite temperature effects

Approach:

- separate system into sub-systems (exploit idea of infinite (homogeneous) reservoirs!)
- calculate properties of sub-systems separately (cheaper…)
- connect by implying equilibrium between sub-systems

Drawback:

- no temporal information („system properties after infinite time“)
- equilibrium assumption



J. Rogal and K. Reuter, *Ab initio atomistic thermodynamics for surfaces: A primer*. In: Experiment, Modeling and Simulation of Gas-Surface Interactions for Reactive Flows in Hypersonic Flights. Educational Notes RTO-EN-AVT-142, Neuilly-sur-Seine (2007).