

Atomistic thermodynamics

How atomistic electronic structure theory can be linked with concepts and techniques from statistical mechanics and thermodynamics

References:

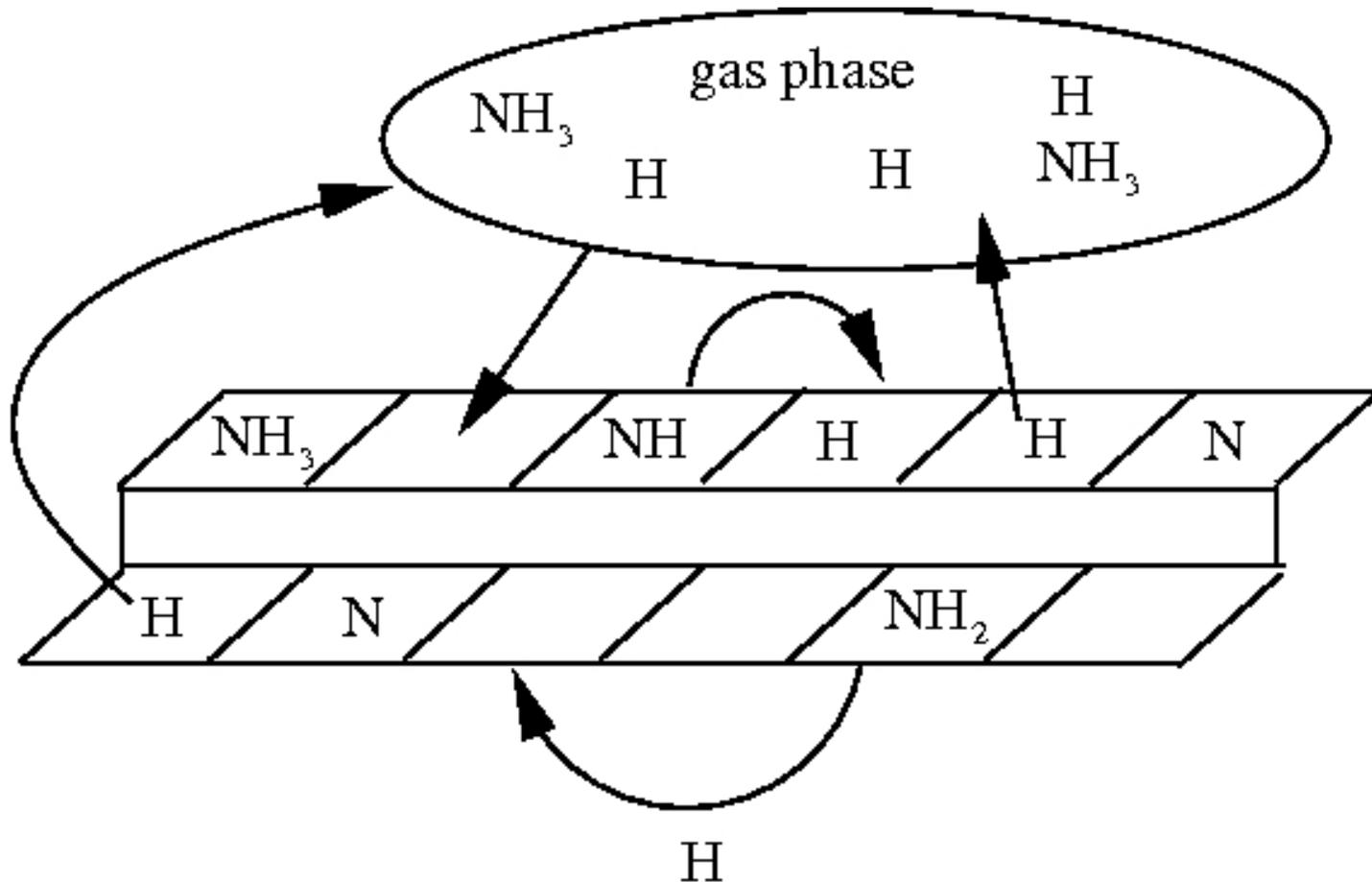
- ♦ K. Reuter et al. in Handbook of Materials Modeling, 149-194, 2005 Springer
- ♦ K. Reuter & M. Scheffler PRB, **65**, 035406 (2001)
- ♦ C. Stampfl Cat. Today **105**, 17 (2005)
- ♦ etc

How the concept works and what it can contribute in practice is illustrated with the case of oxide formation at late transition metal surfaces.

Approximations

Constrained equilibrium:

A surface is considered to be in full thermodynamic equilibrium with one or several separate gas phase reservoirs. No interaction between reservoirs.



Limitations

The main limitation is that its predictive power is limited to the structures that have been explicitly considered and calculated.

 KCM offers greater flexibility !!!

Gibbs free surface energy

To determine the stability of a surface in contact with a gas phase reservoir the surface free energy, γ , is used.

$$\gamma(T, p_i) = \frac{1}{A} \left\{ G^{surf} - \sum_i N_i \mu_i(T, p_i) \right\}$$

G^{surf} is the Gibbs free energy of the solid including the surface, A is the surface area and $\mu_i(T, p_i)$ are the chemical potentials of the various species i (gas and metal) in the system.

In experiments O_2 pressure and temperature are varied 

Consider a surface structure with respect to $\mu_o(p, T)$.

Note that chemical potentials enter in a symmetric way to the equation of γ

Example : RuO₂(110)

Surface free energy:

$$\gamma(T, p) = \frac{1}{2A} \left[G(T, p, N_{Ru}, N_O) - N_{Ru} \mu_{Ru}(T, p) - N_O \mu_O(T, p) \right]$$

If there is enough bulk material

$$\begin{aligned} \mu_{Ru}(T, p) + 2\mu_O(T, p) &= g_{RuO_2}^{bulk}(T, p) \\ \rightarrow \mu_{Ru}(T, p) &= g_{RuO_2}^{bulk}(T, p) - 2\mu_O(T, p) \end{aligned}$$



$$\gamma(T, p) = \frac{1}{2A} \left[G(T, p, N_{Ru}, N_O) - N_{Ru} g_{RuO_2}^{bulk}(T, p) - (2N_{Ru} - N_O) \mu_O(T, p) \right]$$

Depends only on μ_O !

Range of allowed chemical potentials

μ_{O} cannot be varied without bounds.

If μ_{O} becomes too low, all O_2 would leave the sample

$$\max[\mu_{\text{Ru}}(T, p)] = g_{\text{Ru}}^{\text{bulk}}(T, p)$$

Equation

$$\begin{aligned}\mu_{\text{Ru}}(T, p) + 2\mu_{\text{O}}(T, p) &= g_{\text{RuO}_2}^{\text{bulk}}(T, p) \\ \rightarrow \mu_{\text{O}}(T, p) &= \frac{1}{2} \left(g_{\text{RuO}_2}^{\text{bulk}}(T, p) - \mu_{\text{Ru}}(T, p) \right)\end{aligned}$$

Together with the condition $p=0$ and $T=0$

$$\min[\mu_{\text{O}}(T, p)] = \frac{1}{2} [g_{\text{RuO}_2}^{\text{bulk}}(0, 0) - g_{\text{Ru}}^{\text{bulk}}(0, 0)]$$

At the O-rich conditions gas-phase O would condense on the sample

$$\max[\mu_O(T, p)] = g_O^{gas}(T, p)$$

$$\mu_o = 1/2\mu_{O_2} = 1/2 \left\{ E_{O_2}^{tot} + \underbrace{\mu_{O_2}^{vr}(T, p) + k_B T \ln\left(\frac{p_{O_2}}{p_0}\right)}_{\mu_O^{rest}} \right\}$$

At T=0 and p=0 thus

$$\max[\mu_O(T, p)] = \frac{1}{2} E_{O_2}^{total}$$

The Gibbs free energy of formation of the oxide:

$$\Delta G_f(T, p) = g_{RuO_2}^{bulk}(T, p) - g_{Ru}^{bulk}(T, p) - g_{O_2}^{gas}(T, p)$$

The range of oxygen chemical potentials between the theoretical boundaries is

$$\frac{1}{2}\Delta G_f(0, 0) < \mu_O(T, p) - \frac{1}{2}E_{O_2}^{total} < 0$$

Gibbs free energies vs total energies

Helmholtz free energy:

$$F(T, V, N_{Ru}, N_O) = E^{tot}(V, N_{Ru}, N_O) + F^{vib}(T, V, N_{Ru}, N_O)$$

$$F^{vib}(T, V, N_{Ru}, N_O) = E^{vib}(T, V, N_{Ru}, N_O) - TS^{vib}(T, V, N_{Ru}, N_O)$$

E^{vib} and S^{vib} are the vibrational energy and entropy.

F is associated to G as follows:

$$G(T, p, N_{Ru}, N_O) = F(T, p, N_{Ru}, N_O) + pV(T, p, N_{Ru}, N_O)$$

From simple dimensional analysis $[pV/A] = \text{atm } \text{\AA}^3/\text{\AA}^2 \sim 10^{-3} \text{ meV}/\text{\AA}^2$

Since $p < 100 \text{ atm}$, contribution negligible compared to F.



$$G(T, p, N_{Ru}, N_O) = F(T, p, N_{Ru}, N_O)$$

Gibbs free energies vs total energies

The only additional contribution to $G(T,p, N_{Ru}, N_O)$ apart from the DFT total energy is the vibrational term $F^{vib}(T,V,N_{Ru},N_O)$.

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

where

$$F^{vib}(T, \omega) = \hbar\omega \left(\frac{1}{2} + \frac{1}{e^{\beta\hbar\omega} - 1} \right) - kT \left[\frac{\beta\hbar\omega}{e^{\beta\hbar\omega} - 1} - \ln(1 - e^{-\beta\hbar\omega}) \right]$$

Vibrational contribution to the surface free energy stays within $10 \text{ meV}/\text{\AA}^2$ for the O/Ru system. However, this must be checked for an each system

Gibbs free energy of adsorption: O & CO on Pd

To compare the stability of different adsorption structures we calculate

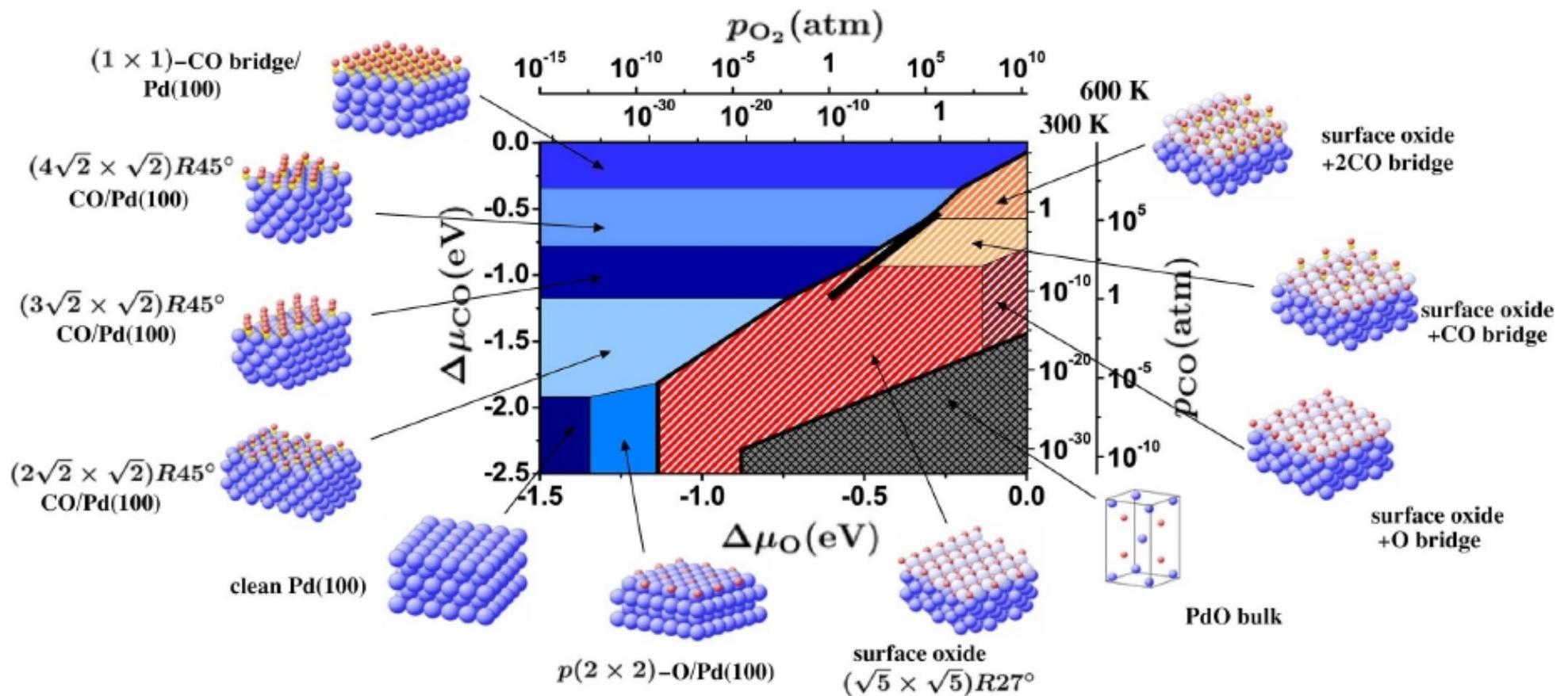
$$\begin{aligned}\Delta G^{ads}(\Delta\mu_O, \Delta\mu_{CO}) &= \gamma_{Pd(100)} - \gamma_{O,CO@Pd(100)} \\ &= \frac{1}{A} \left\{ G_{O,CO@Pd(100)}^{surf} - G_{Pd(100)}^{surf} - \Delta N_{Pd} \mu_{Pd}^{bulk} - N_O \mu_o - N_{CO} \mu_{CO} \right\} \\ &\approx -\frac{1}{A} E_{O,CO@Pd(100)}^{bind} + \frac{N_o}{A} \mu_O^{rest} + \frac{N_{CO}}{A} \mu_{CO}^{rest}\end{aligned}$$

where

$$\mu_o = 1/2 \mu_{O_2} = 1/2 \left\{ E_{O_2}^{tot} + \underbrace{\mu_{O_2}^{vr}(T, p) + k_B T \ln\left(\frac{p_{O_2}}{p_0}\right)}_{\mu_O^{rest}} \right\}$$

$$\mu_{CO} = E_{CO}^{tot} + \underbrace{\mu_{CO}^{vr}(T, p) + k_B T \ln\left(\frac{p_{CO}}{p_0}\right)}_{\mu_{CO}^{rest}} \left\}$$

Surface phase diagram of the Pd(100) in constrained thermodynamic equilibrium with O₂ and CO gas phase



The formation of CO₂ is neglected in the gas phase and on the surface !
 Valid as long as O₂ and CO adsorption and desorption events much more frequent than thereaction.