Ab initio atomistic thermodynamics

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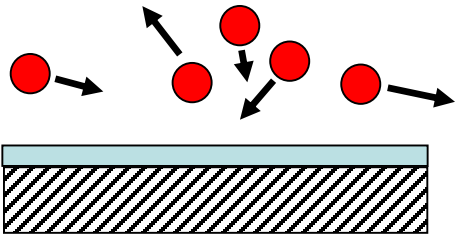
$$\nu = \frac{p}{\sqrt{2\pi mkT}}$$

For T = 300 K, p = 1 atm → ν ~ 10^8 site^{-1} s^{-1}

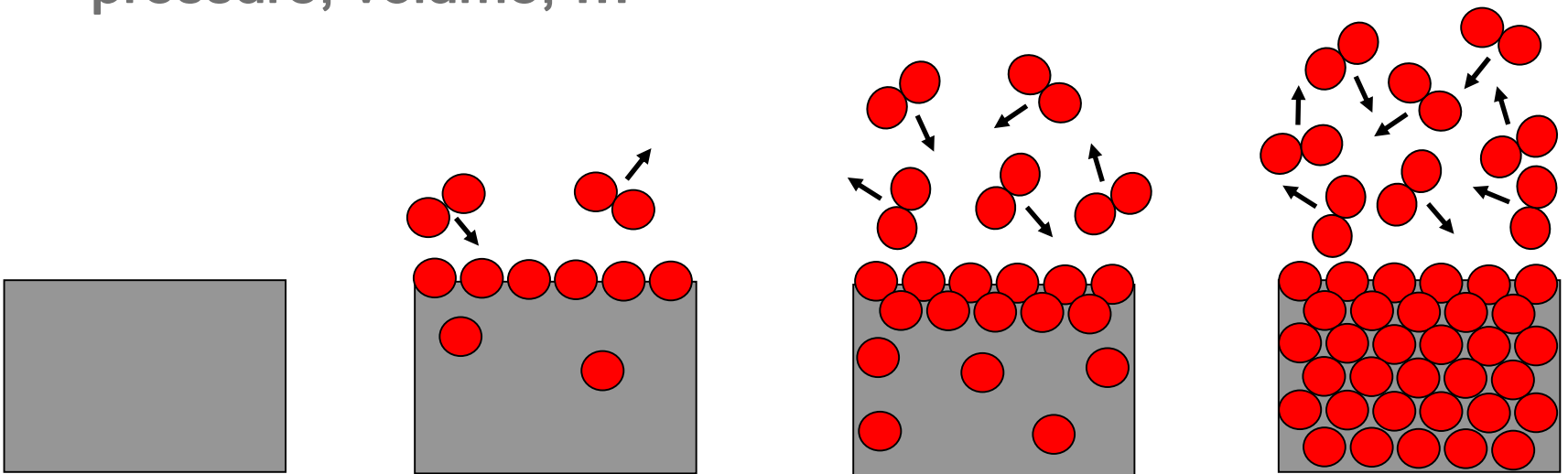Requires $p \leq 10^{-12}$ atm to keep a "clean" surface clean; surface can also lose atoms

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

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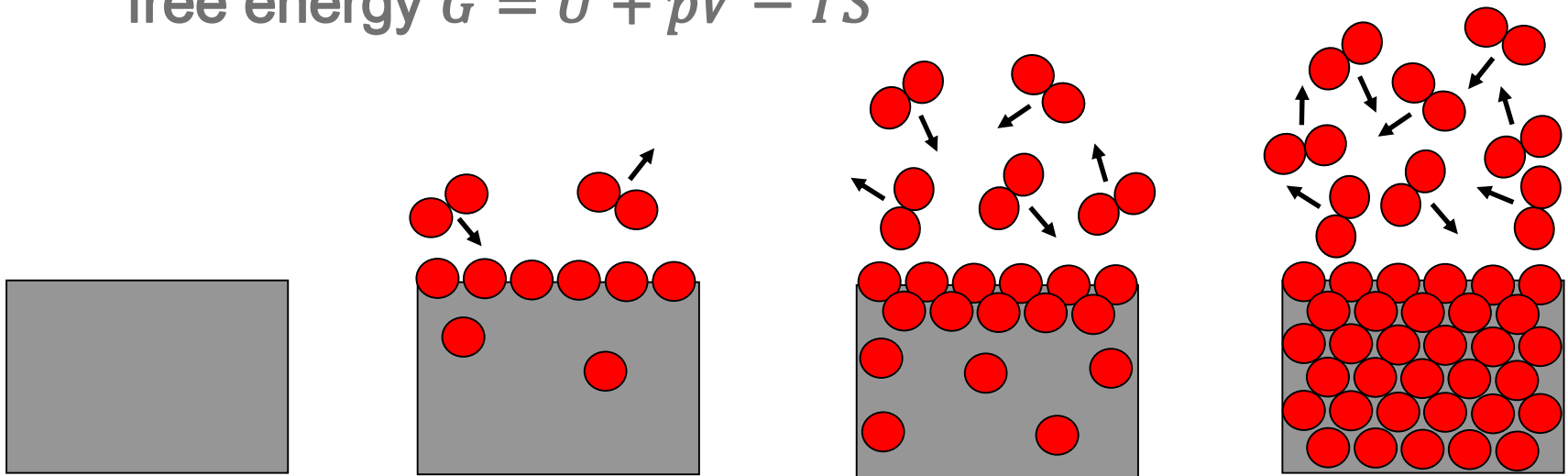
Thermodynamics

❏ **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 $G = U + pV - TS$

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 $W \to \max$, so that $S \to \max$; (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 $$P_i = \frac{e^{-E_i/kT}}{Z}, \quad Z = \sum_i e^{-E_i/kT}, \quad \sum_i P_i = 1$$

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 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: $W = \frac{N!}{N_1!(N-N_1)!}\frac{(N-N_1)!}{N_2!(N-N_1-N_2)!}\ldots = \frac{N!}{N_1!N_2!\ldots}$ where N_1, N_2,… 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**

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

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

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

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

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

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

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

Thermodynamics

□ **Statistical thermodynamics**

Practical example: surface free energy

$$\mu_{O_2}(T, p_{O_2})$$

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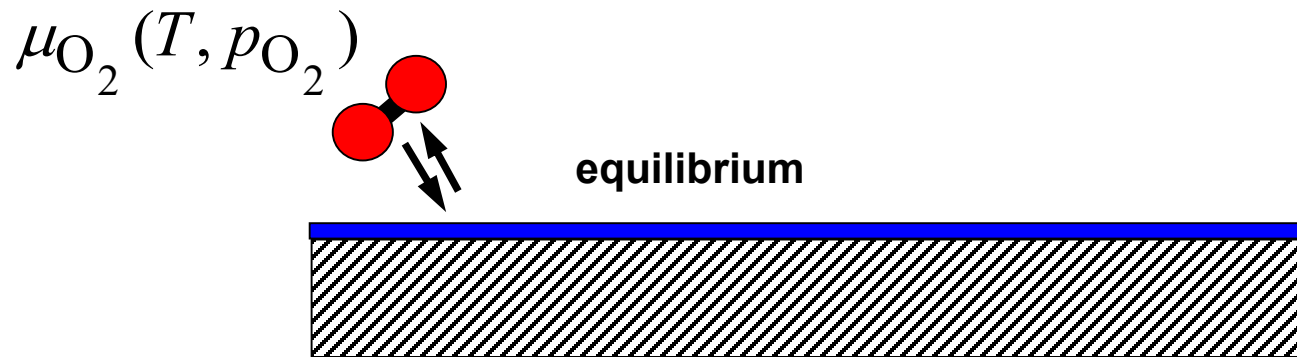
Change in Gibbs free energy upon addition of O to the surface: $\Delta G = G_{surf}(N_O + 1) - \left(G_{surf}(N_O) + \frac{1}{2}\mu_{O_2} \right)$ since $\mu_O = \frac{1}{2}\mu_{O_2}$

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

Thermodynamics

□ **Statistical thermodynamics**

Practical example: surface free energy

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

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

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

$\mu_O(T, p)$ - ?

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**

$$\mu(T, p) = \frac{\partial}{\partial N}\left(-NkT\ln(z_{transl}) + kT\ln N! - NkT\ln(z_{rot}) - \right.$$

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

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

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

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 is the bond length

$\mu_{rot} \approx -kT\ln\left(\frac{2kTI}{\sigma\hbar^2}\right)$, required input - rotational constant $B_0 = \frac{\hbar^2}{2I}$ (calculated or from microwave spectroscopy)

Thermodynamics

☐ **Statistical thermodynamics**

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

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

For a diatomic molecule $\mu_{vib} = \frac{\hbar\omega}{2} + kT\ln\left(1 - e^{-\hbar\omega/kT}\right)$ 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 $\mu(T, p) : \mu(T, p) = E_0 + \Delta\mu(T, p)$
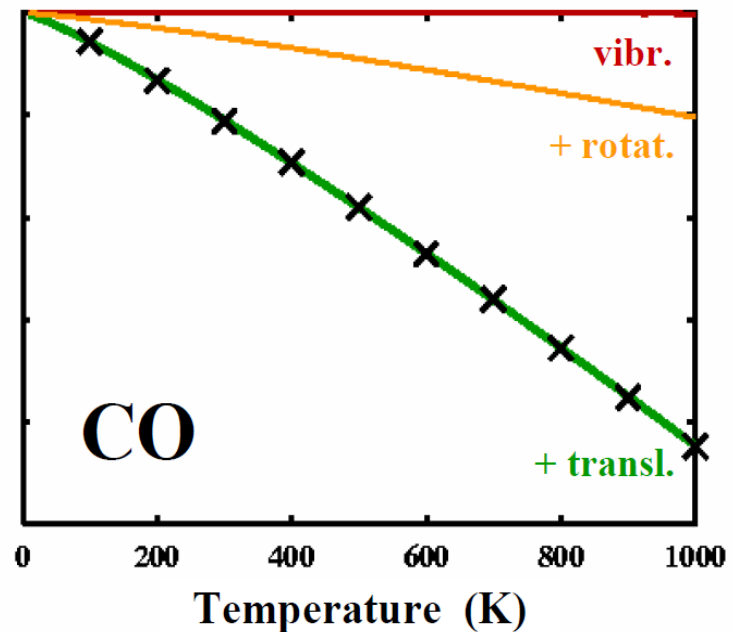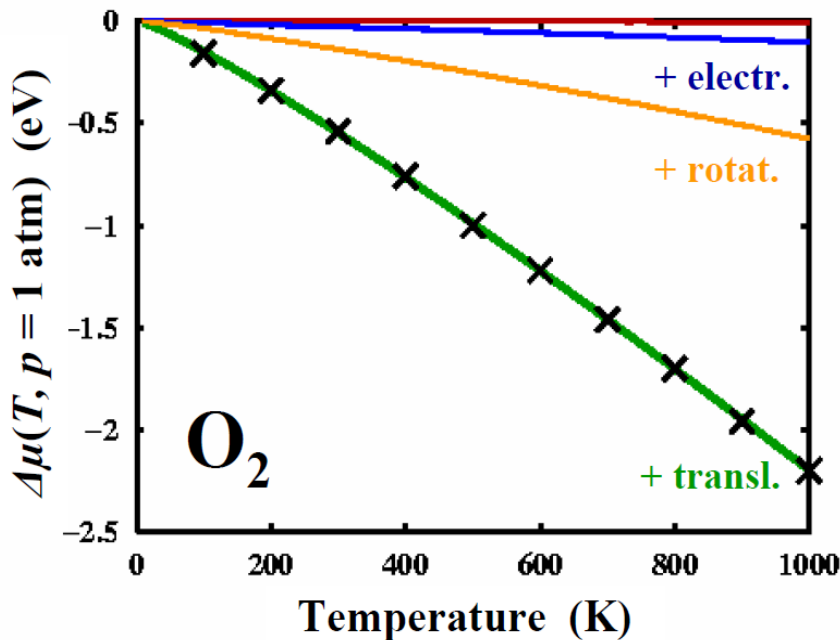
Alternatively: $\Delta\mu(T, p) = \Delta\mu(T, p^{O}) + k_{B}T\ln(p / p^{O})$

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

Thermodynamics

☐ *Ab initio* **atomistic thermodynamics**

$$\mu_{O_2}(T, p_{O_2})$$
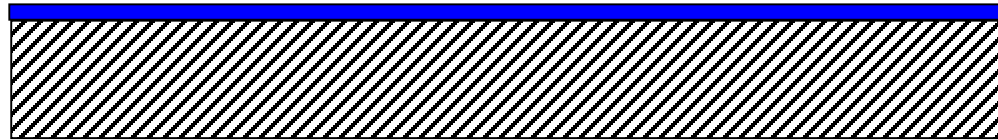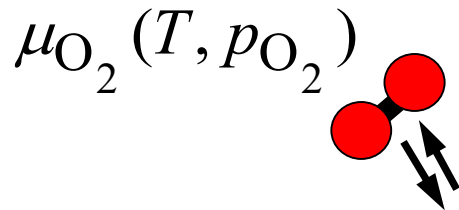
$$\Delta\gamma(N_O, T, p) = \frac{1}{A}\left[\Delta E_{surf} + \Delta U_{vib} - T\Delta S_{vib} - T\Delta S_{conf} + p\Delta V - \mu_O\Delta N_O\right]$$

electronic structure calculations

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

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

Thermodynamics

☐ **_Ab initio_ atomistic thermodynamics**

Example: Metal surface in contact with O_2 gas

surface

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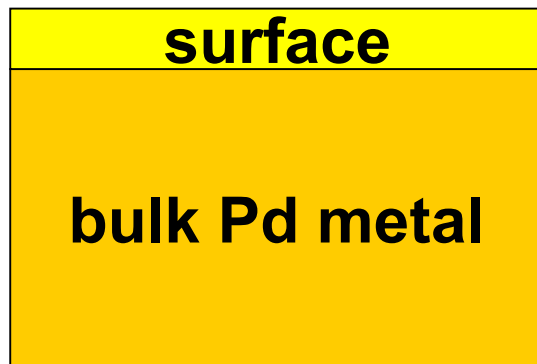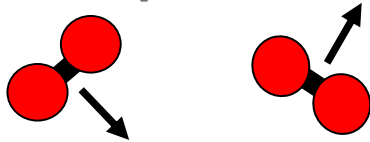
Reservoir: $\mu_O\left(T, p_{O_2}\right)$ from ideal gas, $N_O^{ref} = 0$ (bare metal surface is the reference system), $\frac{1}{2}E_{O_2}$ is the reference for the chemical potential of O: $\mu_O = \Delta\mu_O + \frac{1}{2}E_{O_2}$

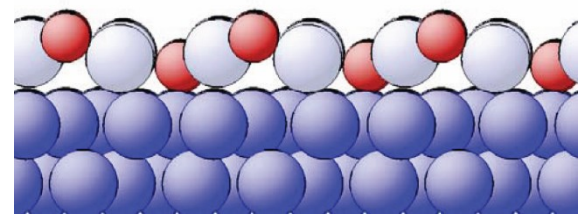Neglect for now ΔF_{vib} and $T\Delta S_{conf}$

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

Example: Pd(100)

$$\Delta\gamma(T, p_{O_2}) = \frac{1}{A}\Delta E_{surf}(N_O) - \frac{1}{A}N_O\Delta\mu_O(T, p_{O_2})$$
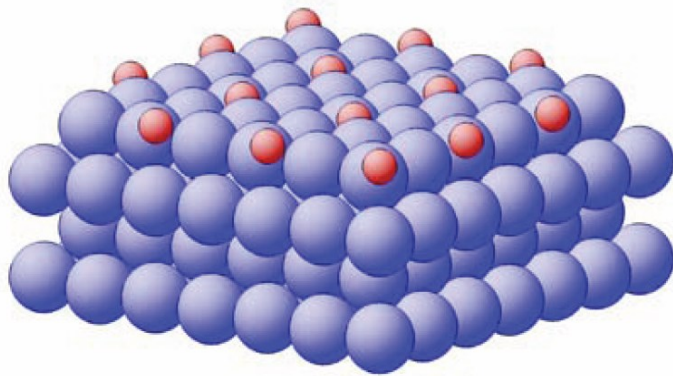
p(2x2) O/Pd(100)

($\sqrt{5}$x$\sqrt{5}$)*R*27° PdO(101)/Pd(100)

M. Todorova *et al.*, Surf. Sci. 541, 101 (2003); K. Reuter and M. Scheffler, Appl. Phys. A 78, 793 (2004)
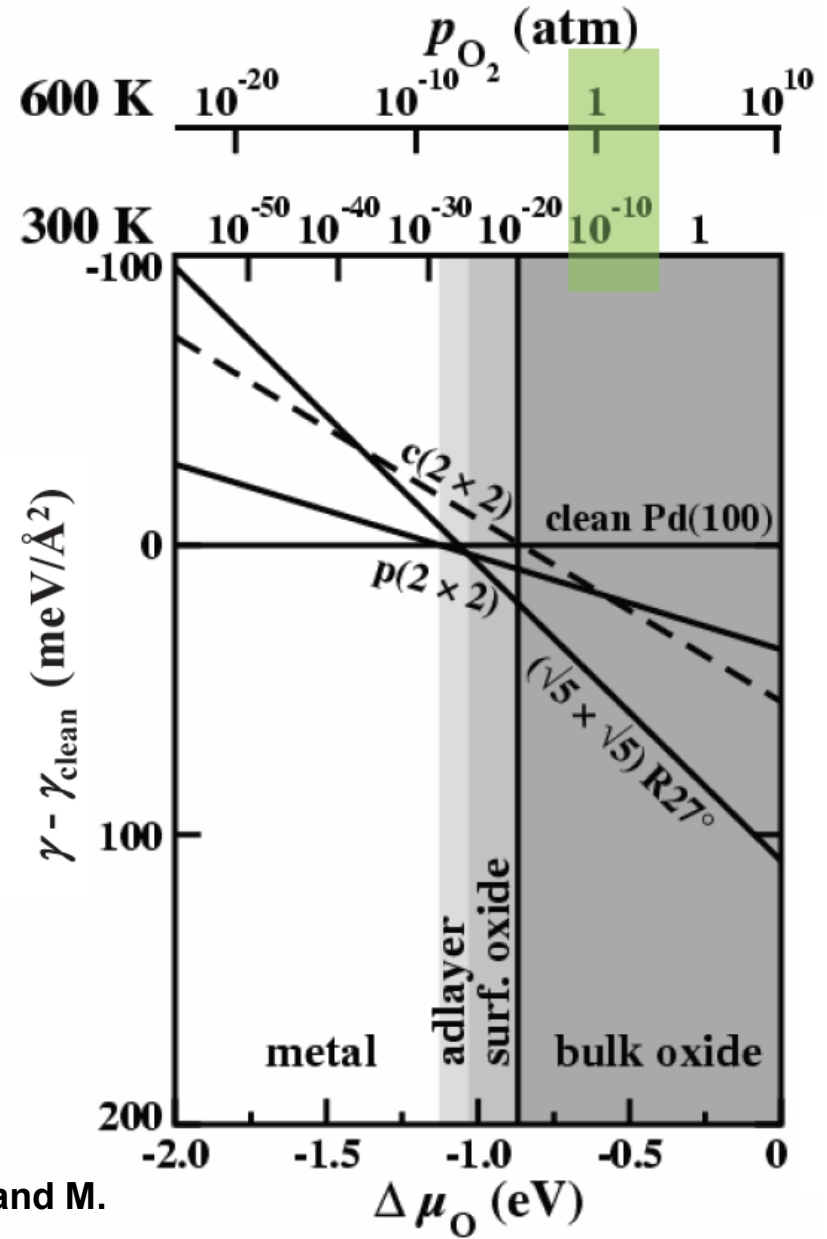
# First-principles atomistic thermodynamics: constrained equilibria

$\mu_{O_2}(T, p_{O_2})$

$\mu_{CO}(T, p_{CO})$

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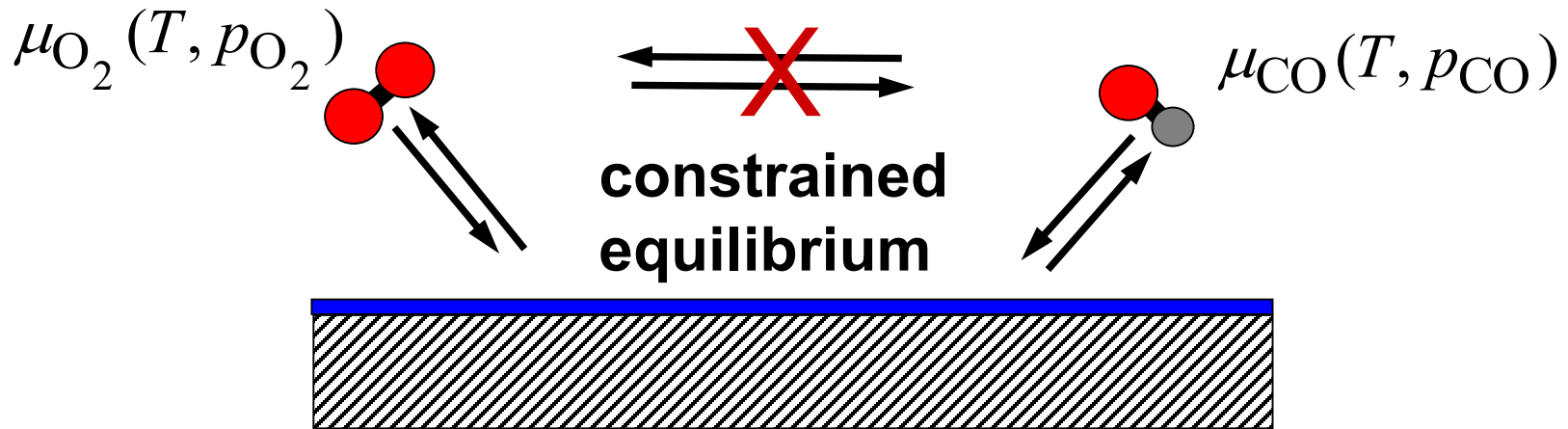
$$\Delta\gamma(T, p_{O_2}) = \frac{1}{A}\left[E_{surf}(N_O, N_{CO}) - E_{surf}^{ref} - N_O\frac{1}{2}E_{O_2} - N_{CO}E_{CO}\right]$$

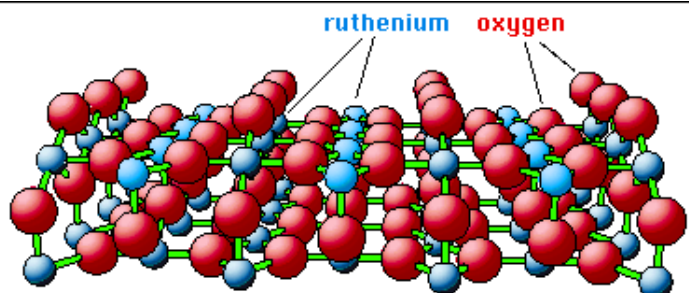$$-\frac{1}{A}N_O\Delta\mu_O(T, p_{O_2}) - \frac{1}{A}N_{CO}\Delta\mu_{CO}(T, p_{CO})$$

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)
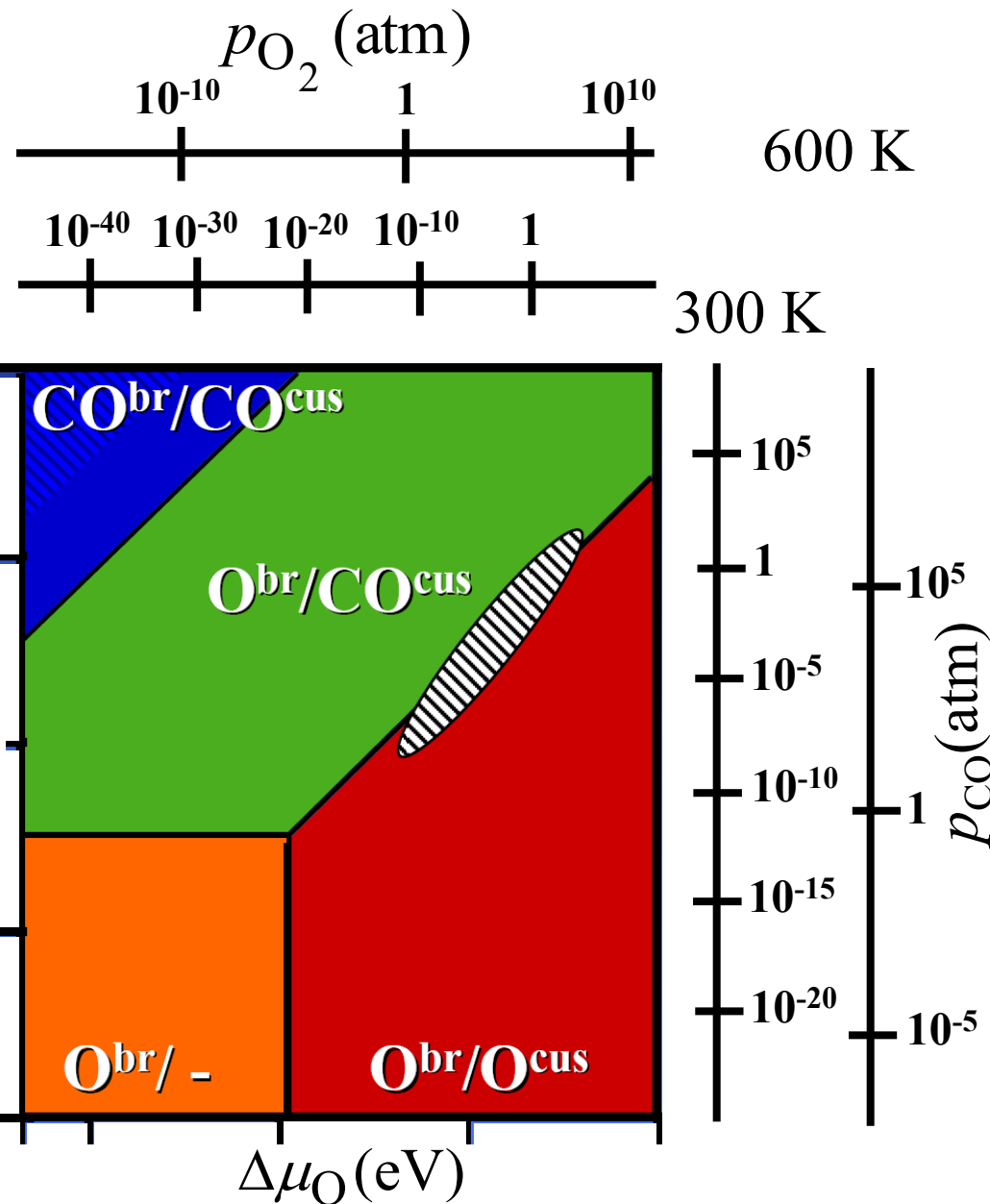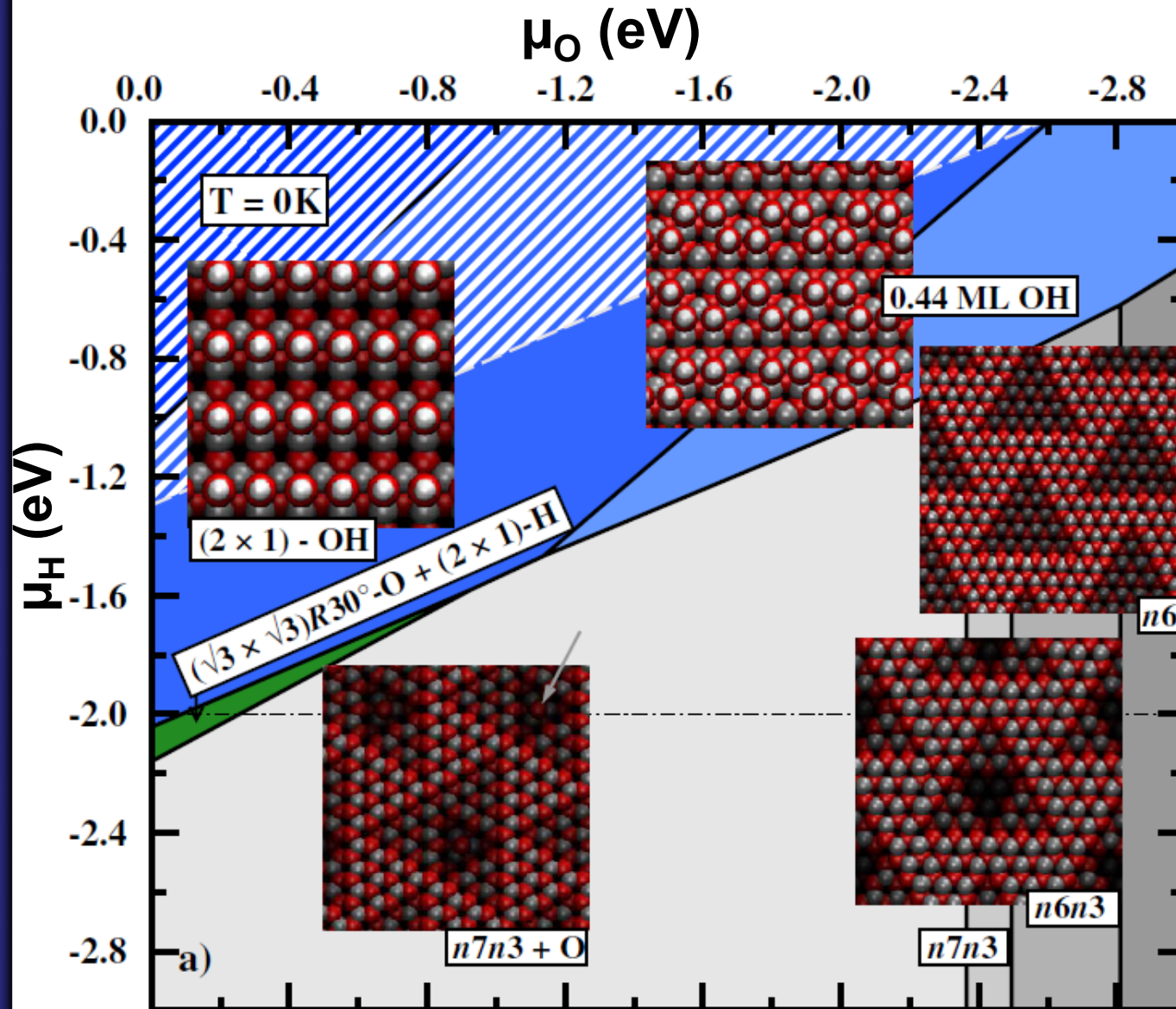
Surface phase diagrams

CO^{br}/CO^{cus}

O^{br}/O^{cus}

O^{br}/CO^{cus}

$O^{br}/-$

γ (meV/Å^2)

$\Delta\mu_O$ (eV)

$\Delta\mu_{CO}$ (eV)
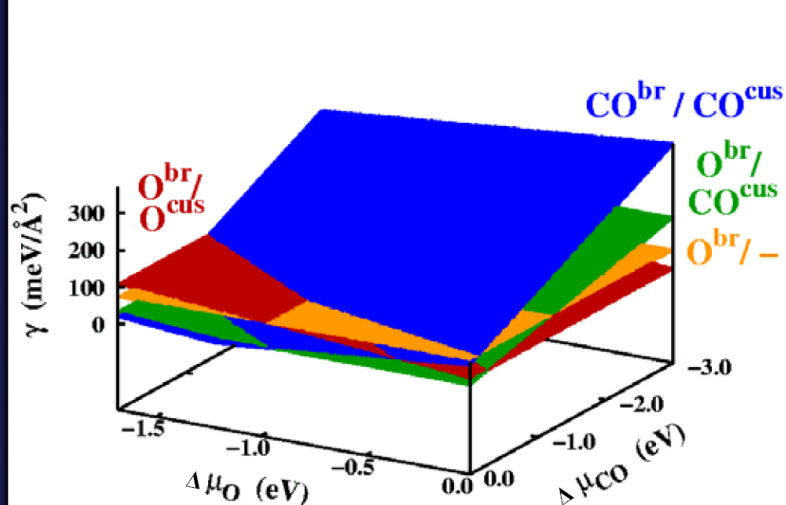
CO oxidation on RuO$_2$(110)

ruthenium   oxygen

IAP, TU Wien

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

p_{O_2} (atm)

| 10^{-10} | 1 | 10^{10} | 600 K |

| 10^{-40} | 10^{-30} | 10^{-20} | 10^{-10} | 1 | 300 K |

CO^{br}/CO^{cus}

O^{br}/CO^{cus}

$O^{br}/-$

O^{br}/O^{cus}

$\Delta\mu_{CO}$ (eV)

$\Delta\mu_O$ (eV)

10^5

1

10^{-5}

10^{-10}

10^{-15}

10^{-20}

10^5

1

10^{-5}

p_{CO} (atm)

When vibrations do matter

ZnO (0001) surface phase diagram in H_2O-O_2 atmosphere – no vibrations

No structure with (2x2) periodicity as seen at the ZnO(0001) surface annealed in a dry oxygen atmosphere (containing at maximum 2 ppm water)

μ$_O$ (eV)

μ$_H$ (eV)

T = 0K

0.44 ML OH

(2 × 1) - OH

($\sqrt{3} \times \sqrt{3}$)R30°-O + (2 × 1)-H

n6

n7n3 + O

n6n3

n7n3

a)

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)
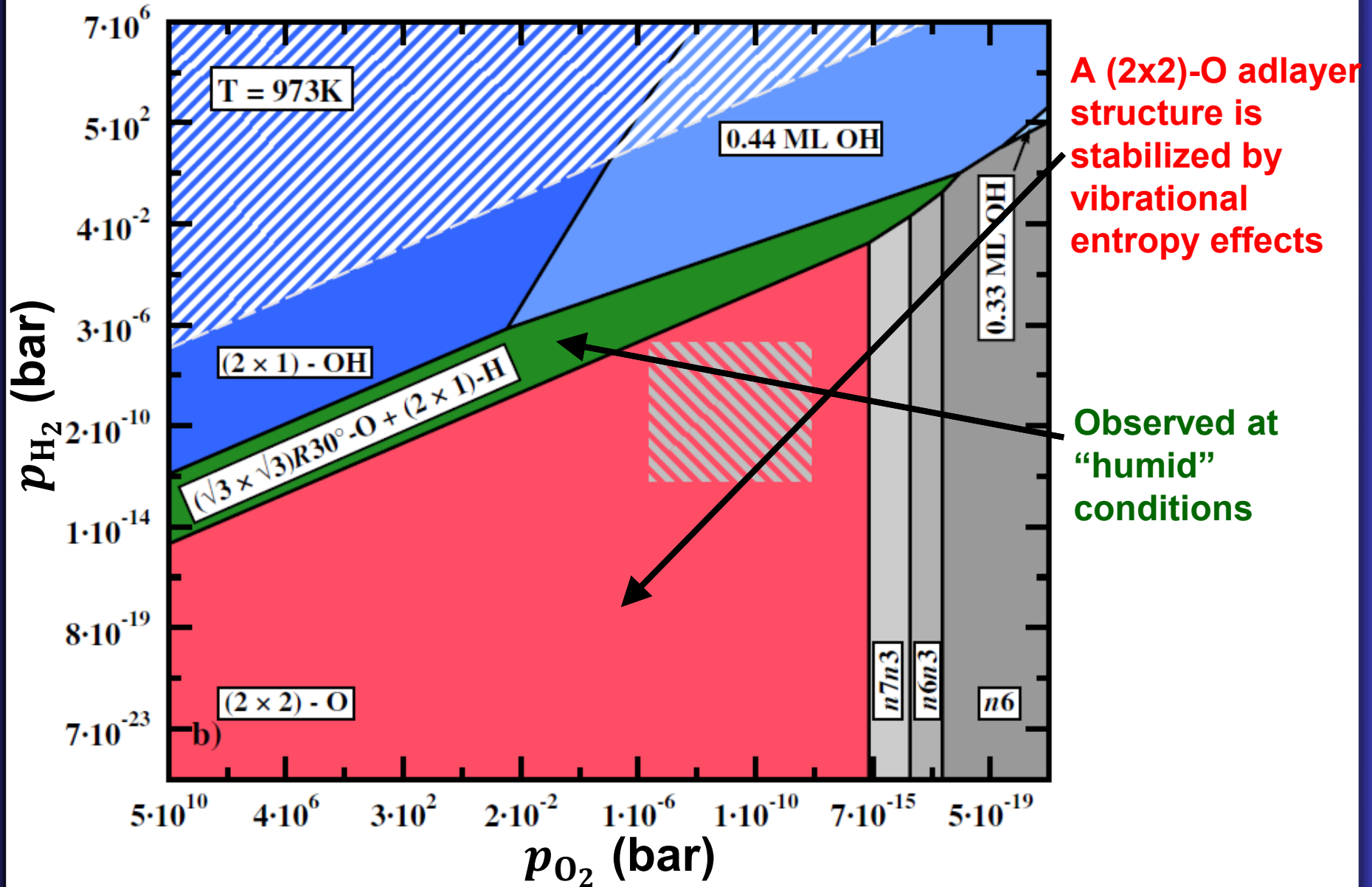
Thermodynamics of Defects

☐ **Very small concentrations of defects can significantly alter materials properties**

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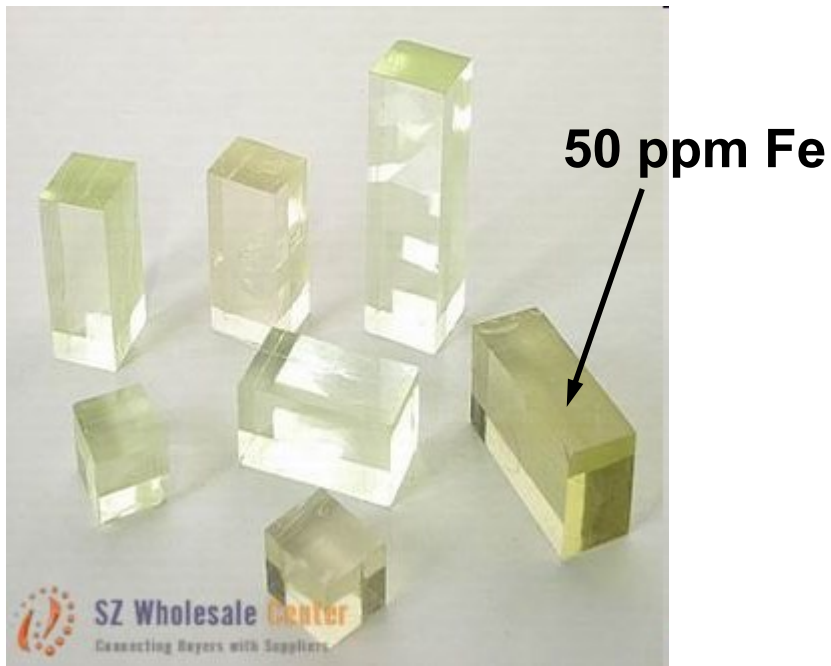
Small concentration of Fe impurities are visible by naked eye in intrinsically transparent MgO

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

"My precious!": Perfect defected gems

Cr:Al$_2$O$_3$

V:Al$_2$O$_3$

Fe:Al$_2$O$_3$

Fe:Al$_2$O$_3$

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

Typical concentrations: 100-10000 ppm

Fe,Ti:Al$_2$O$_3$

Entropy

$$G = U + pV - TS$$

$$S = k \ln W$$
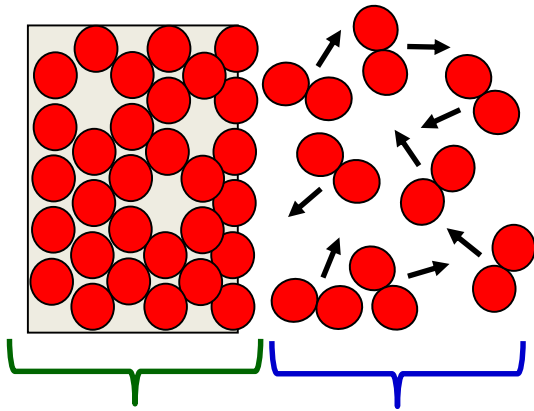
W **– number of microstates**

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

$$G = [U + pV - T(S - S_{\text{config}})] - TS_{\text{config}} = \tilde{G} - TS_{\text{config}}$$
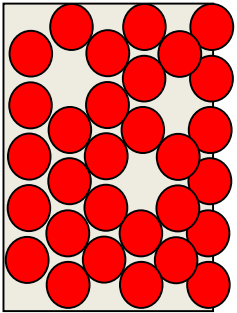
N **equivalent defect sites in the sold**

n **defects**

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

Stirling's formula:

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

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

Good approximation only on a macroscopic scale

Defect concentration

Minimize the free energy of the system with respect to the number of defects
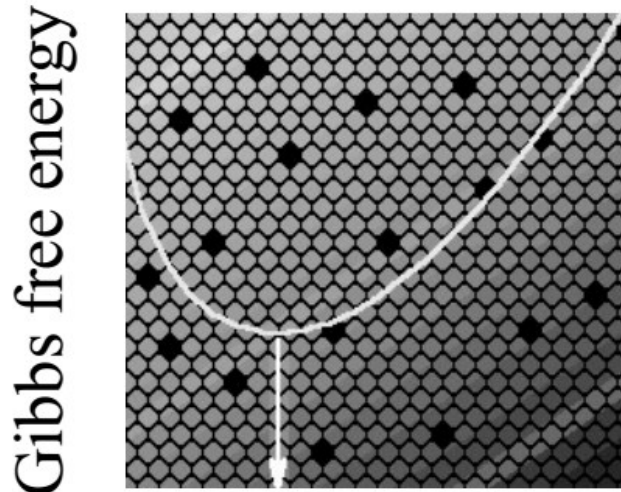
Gibbs free energy vs. Vacancy concentration

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

If defects do not interact:

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

$$\frac{n}{N} << 1 \Leftrightarrow \exp\left(\Delta G_f / kT\right) >> 1$$
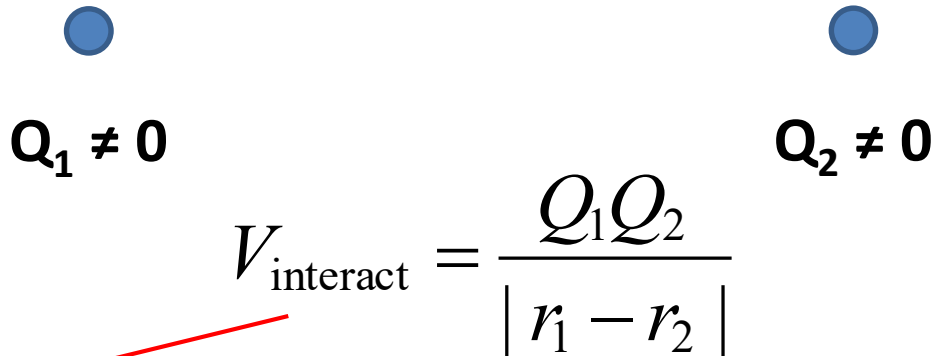
$$\frac{n}{N} \approx \exp\left(-\Delta G_f(T, p) / kT\right) \text{ – \textbf{textbook formula}}$$

Charged defects and charge compensation

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

for non-interacting defects

But can charged defects be considered as non-interacting?!

Q$_1$ ≠ 0 **Q$_2$ ≠ 0**

$$V_{\text{interact}} = \frac{Q_1 Q_2}{|r_1 - r_2|}$$
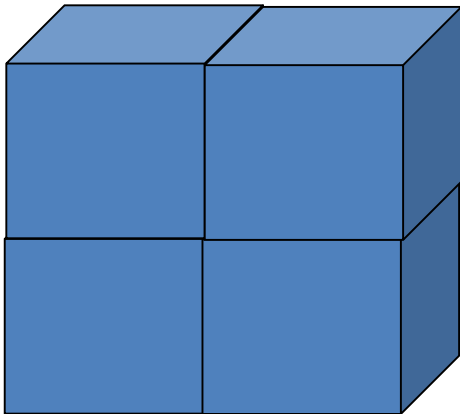
Coulomb interaction – long-range!

Charged defects and charge compensation

$Q_1 \neq 0$ $Q_2 \neq 0$

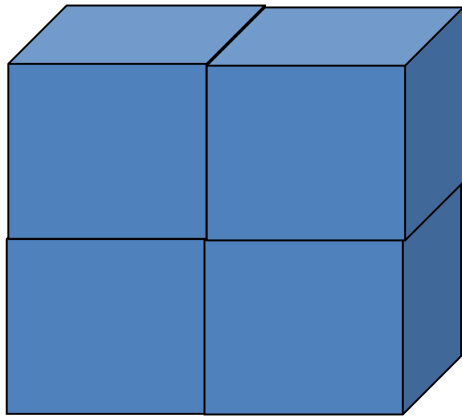$$V_{\text{interact}} = \frac{Q_1 Q_2}{|r_1 - r_2|}$$

For a system of charges:

$$V_{\text{interact}} = \frac{1}{2} \sum_{i \neq j} \frac{Q_i Q_j}{|r_i - r_j|}$$

In the thermodynamic limit ($N \rightarrow \infty$) the electrostatic energy of charges with any finite concentration *diverges*
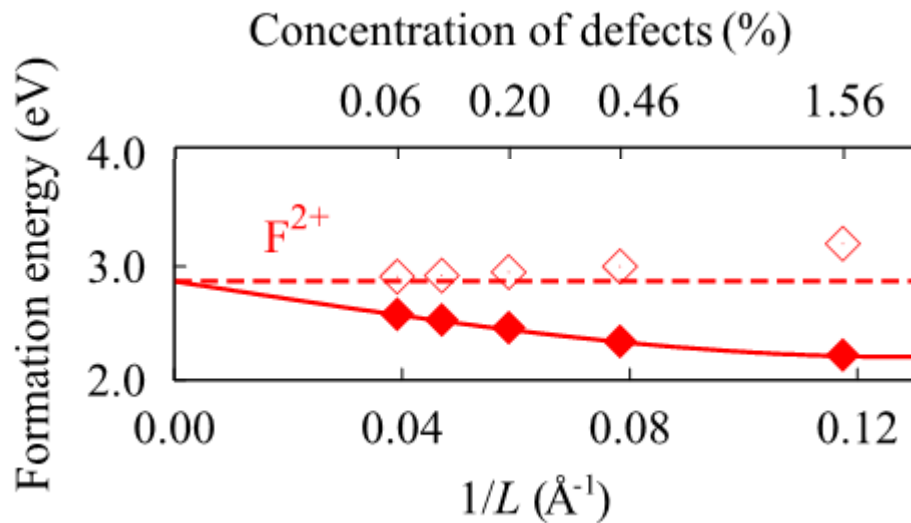
Charged defects *must be compensated* in realistic materials

Charged defects and charge compensation

For a system of charges:

$$V_{\text{interact}} = \frac{1}{2} \sum_{i \neq j} \frac{Q_i Q_j}{|r_i - r_j|}$$

In the thermodynamic limit ($N \rightarrow \infty$) the electrostatic energy of charges with any finite concentration *diverges*

Typical dependence of the defect formation energy as a function of unit cell size

Charged defects and charge compensation
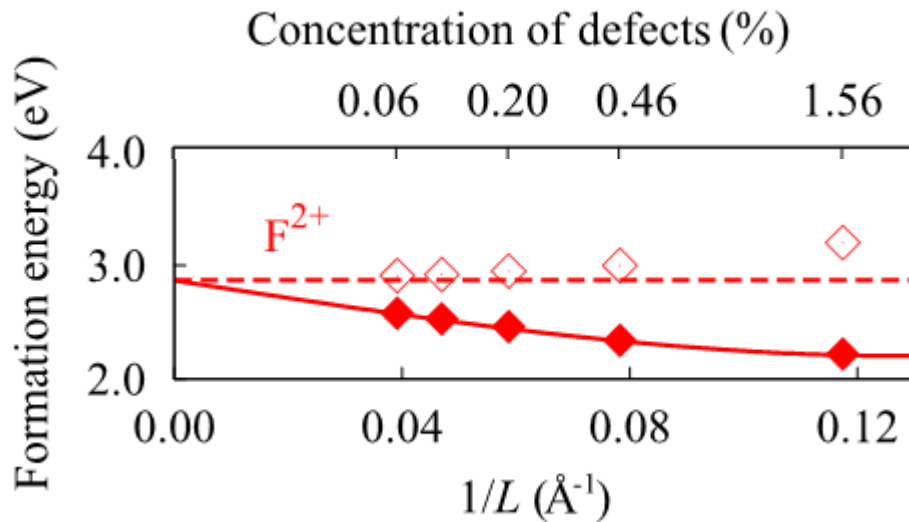
Typical dependence of the defect formation energy as a function of unit cell size

In standard periodic calculations the charge per unit cell is compensated by a uniform background charge (occurs naturally as a regularization of the Ewald summation)

The compensated defects interact much weaker with each other

But they do interact strongly with the compensating charge (~1/L)

Local and global effects of doping

In realistic semiconductors, charged defects can be compensated by the *depletion* of charge carriers (electrons or holes)

electrons occupying hole states (localized or not)
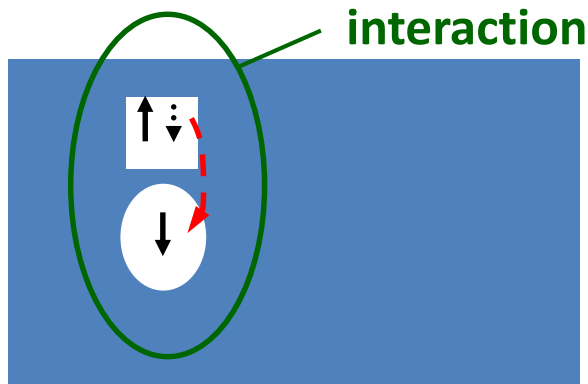
interaction

Local effect of doping (chemical bond formation, local relaxation)
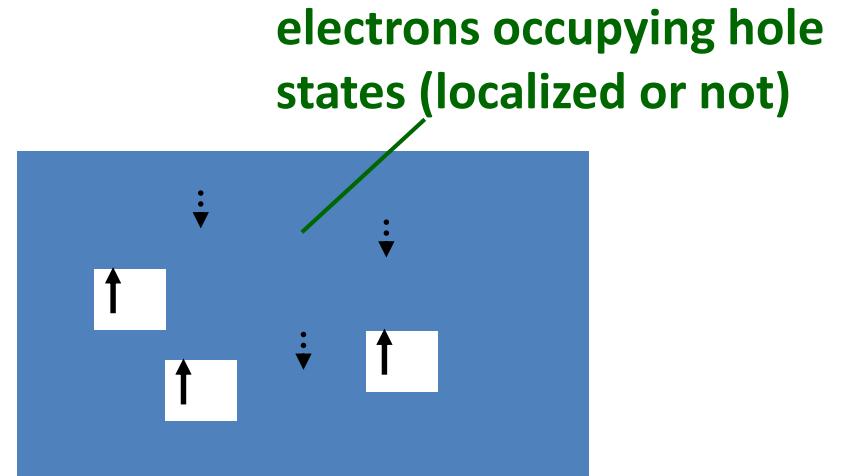
Global effect of doping (interaction with the compensating charge)

Formation energy and concentration of charged defects depend strongly on the distribution of the defects and the compensating charge

Charged defects in a doped material

$$\Delta G(n) = n \Delta G_f (n \to 0) + \frac{1}{2} \varepsilon_0 \int \varepsilon(\mathbf{r}) |\mathbf{E}|^2 d^3 r - T S_{\text{config}}(n)$$

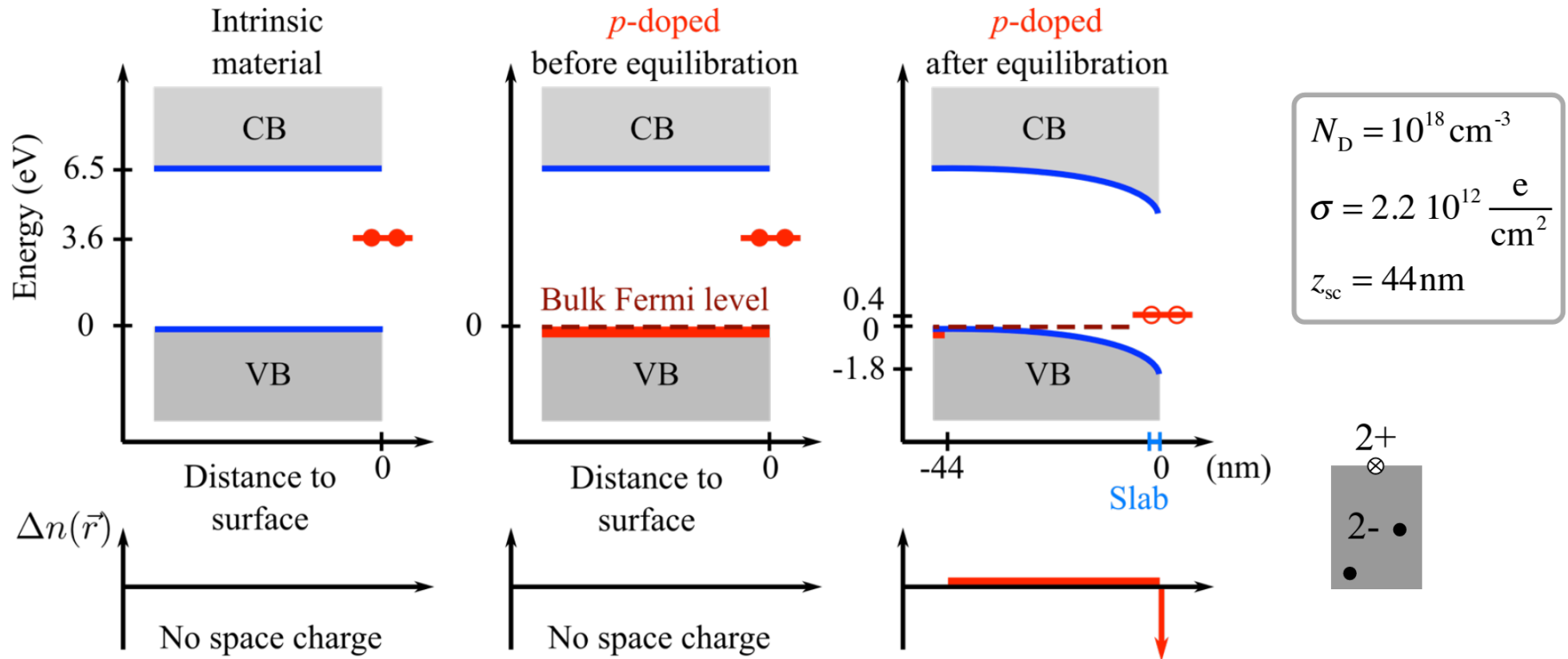**formation energy
in the dilute limit**

**electrostatic energy
at finite *n***

$$S_{\text{config}} = k \ln Z + \frac{U}{T}$$

The charged defects are screened by the compensating charge:

$$S_{\text{config}} \approx k \ln \frac{N!}{n!(N-n)!}$$

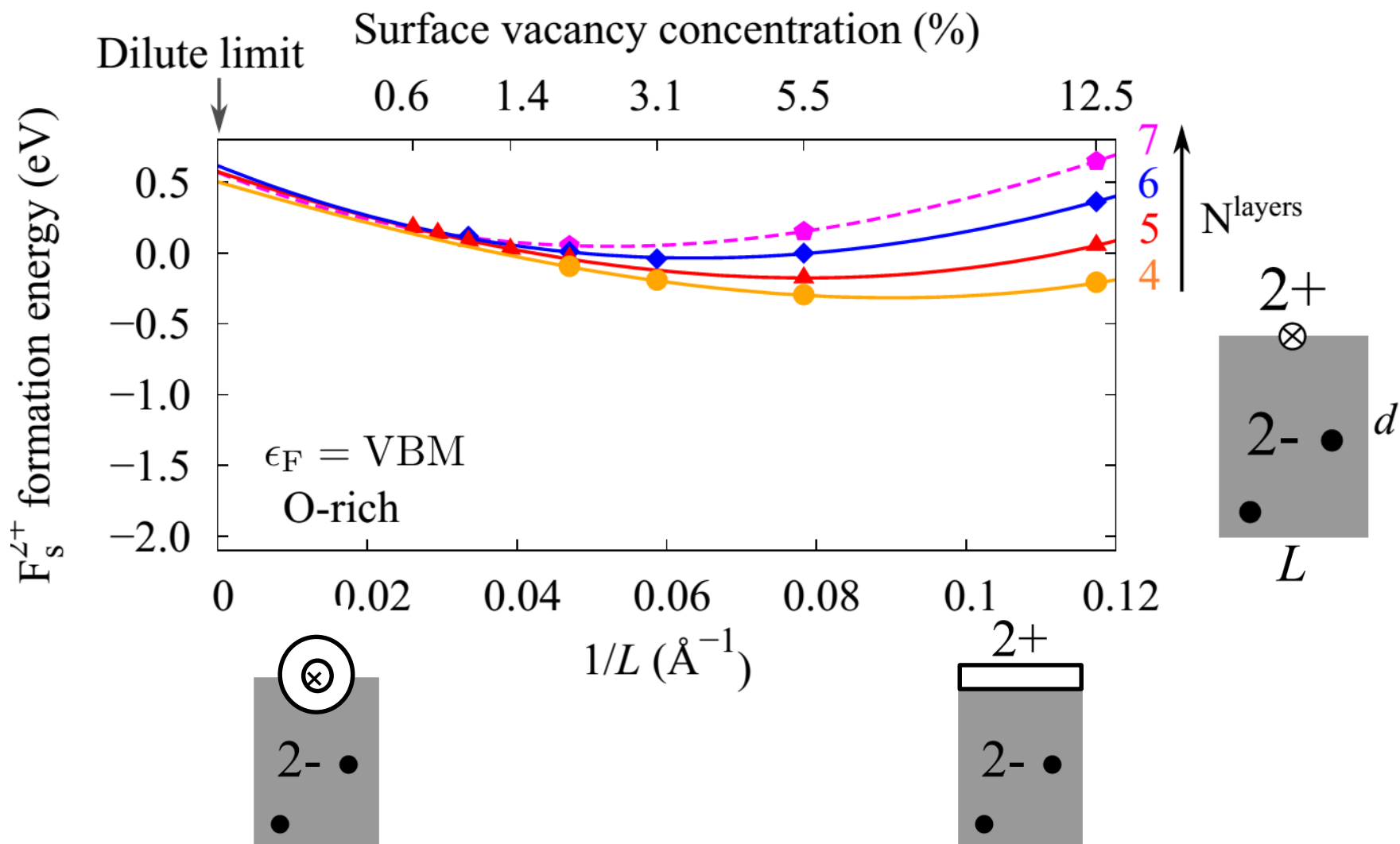# Space charge formation and band bending

Space charge region $z_{SC} = \sigma/eN_D$ causes band bending and electric field

N_D -- dopant concentration
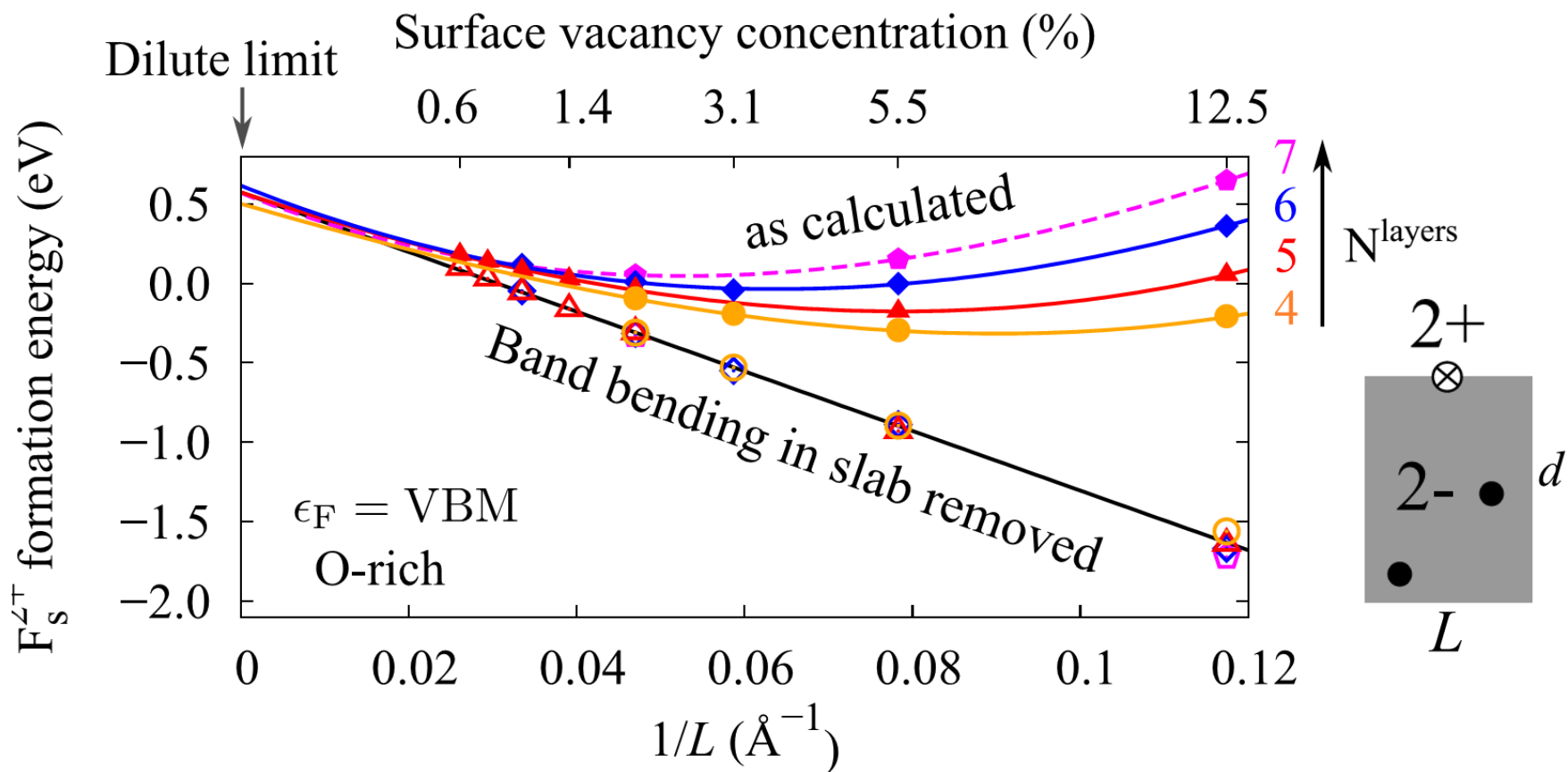
σ -- surface charge due to charged vacancies

Band bending

$$\Delta G_{\text{f}}^{\text{VCA}}(\sigma, d) = E_{\text{vac}}^{q}(\sigma, d)(+q\varepsilon_{\text{VBM}}) - E_{\text{host}}(\sigma, d) + \frac{1}{2}E_{O_2}$$
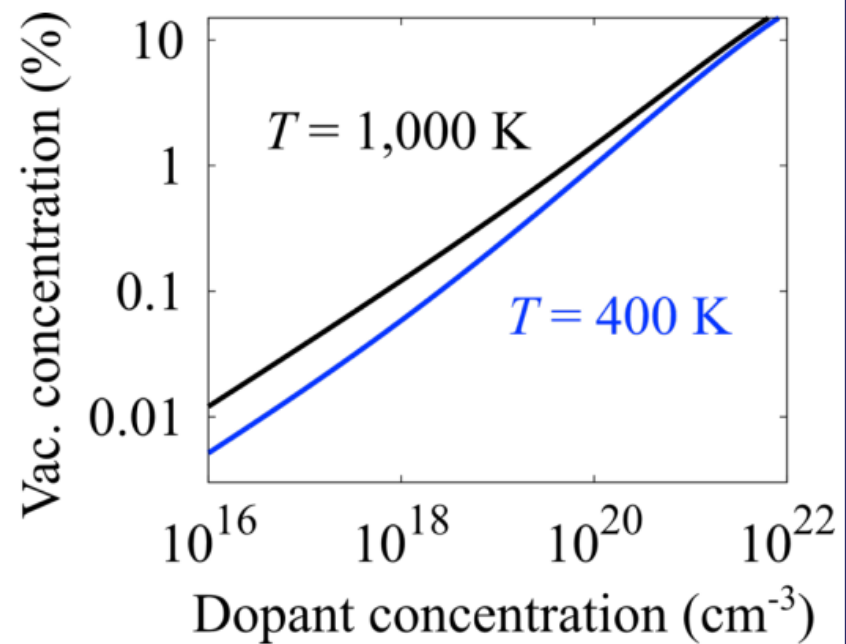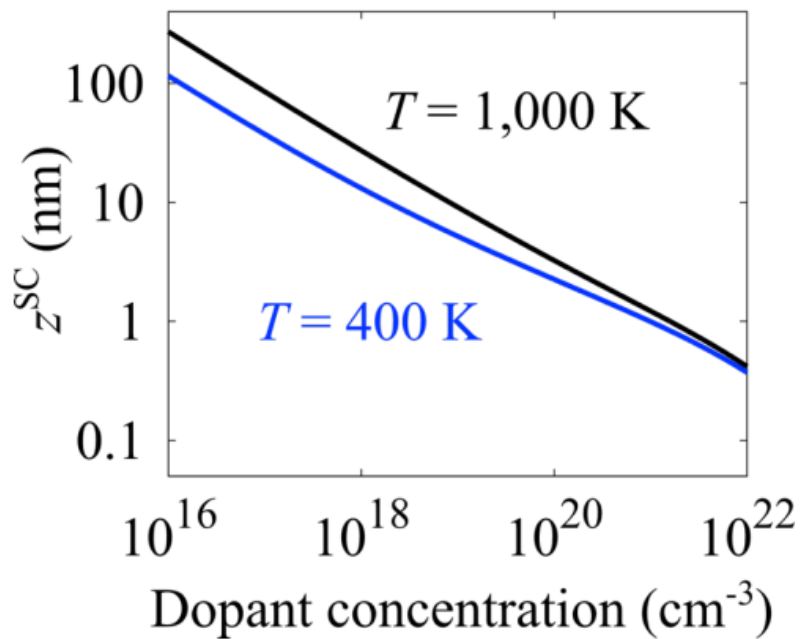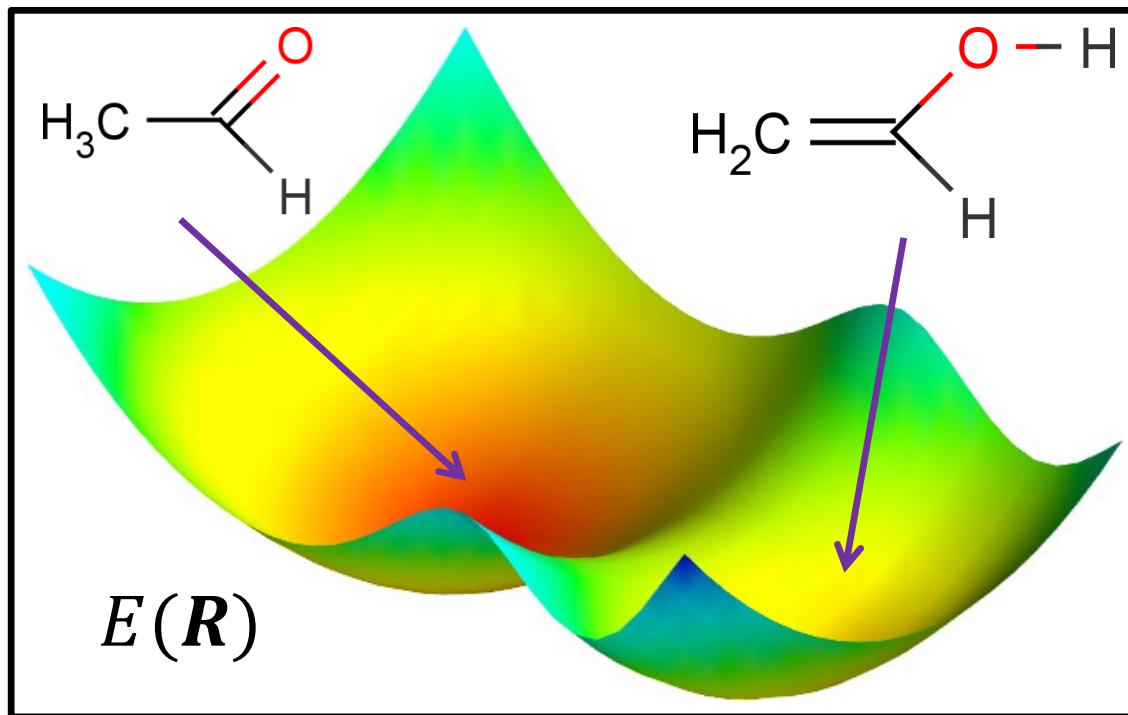
Band bending

$$\Delta G_{\mathrm{f}}^{\mathrm{VCA}}(\sigma,d) = E_{\mathrm{vac}}^{q}(\sigma,d)(+q\varepsilon_{\mathrm{VBM}}) - E_{\mathrm{host}}(\sigma,d) + \frac{1}{2}E_{\mathrm{O_2}}$$

$$\frac{1}{2}\varepsilon\varepsilon_0 \int |\mathbf{E}|^2 d^3r = -C\sqrt{|\sigma|} + qE^{\mathrm{SC}}(d), \quad E^{\mathrm{SC}}(d) = \frac{e|\sigma|}{6\varepsilon\varepsilon_0}d$$

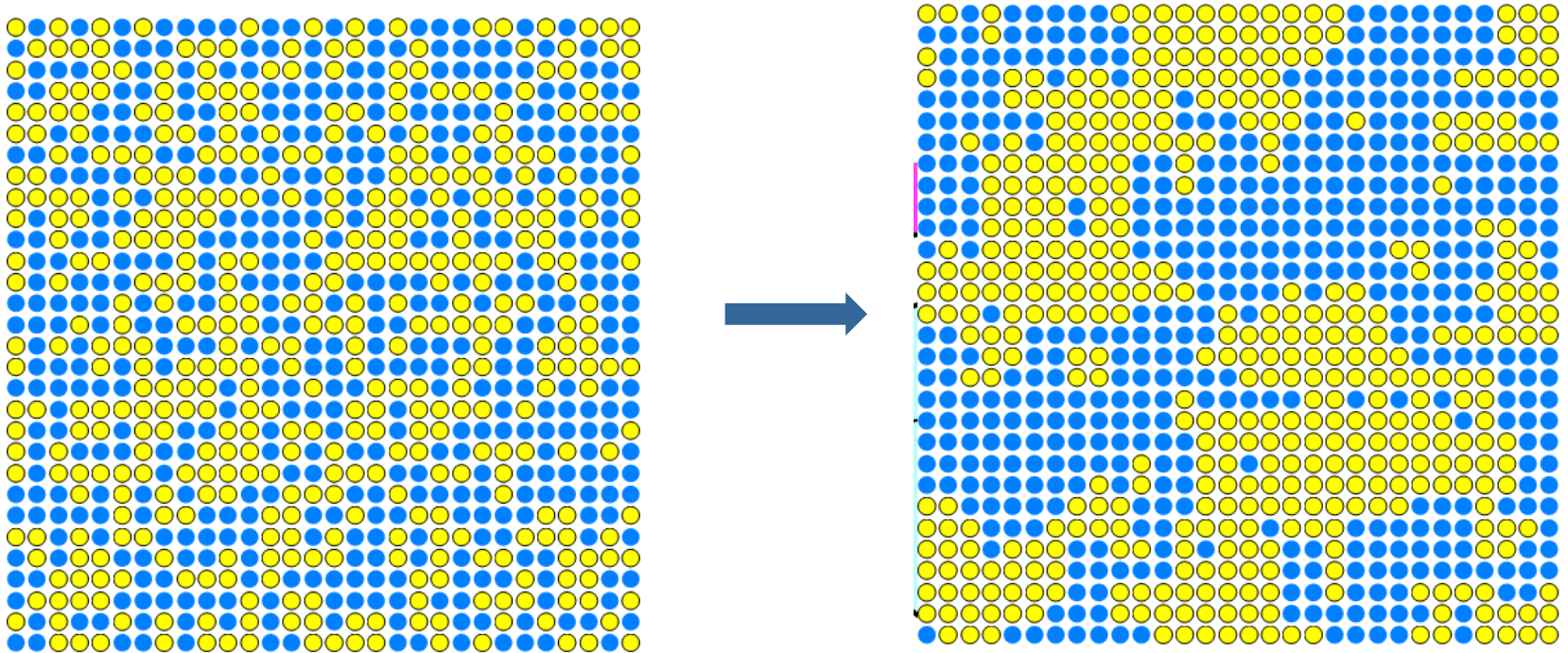# F^{2+} concentration at p-MgO(001)

Sampling configurations

□ **Coarse-graining potential-energy surface (PES)**

Sampling configurations: cluster expansion

☐ **Coarse-graining potential-energy surface (PES)**

Phase transformation in an alloy or adsorbate layer at a surface

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 prominant examples

- Doping should be considered as a thermodynamic variable, along with temperature and pressure

The End ...