

Advanced Materials Modeling:

Statistical mechanics and *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

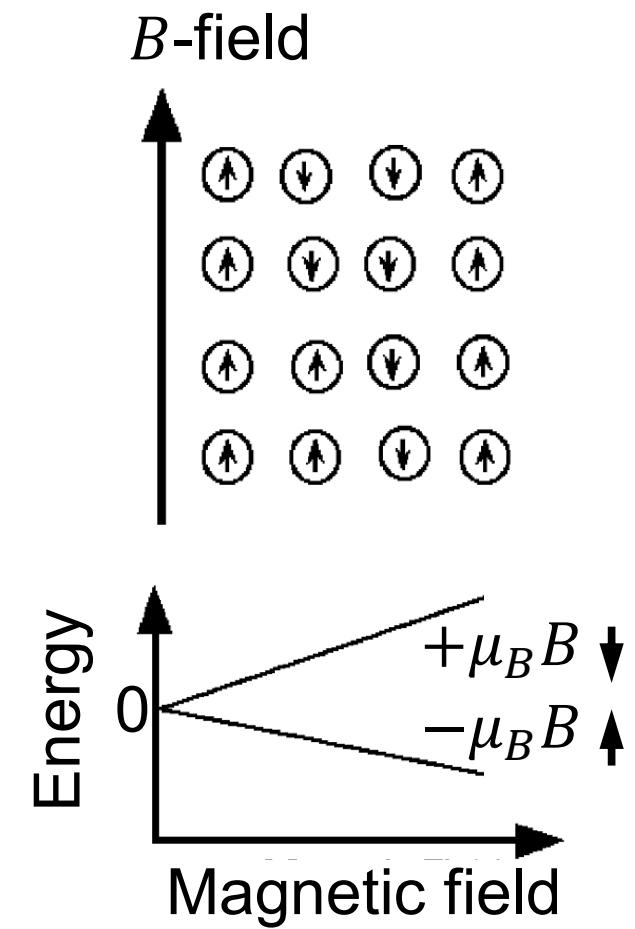
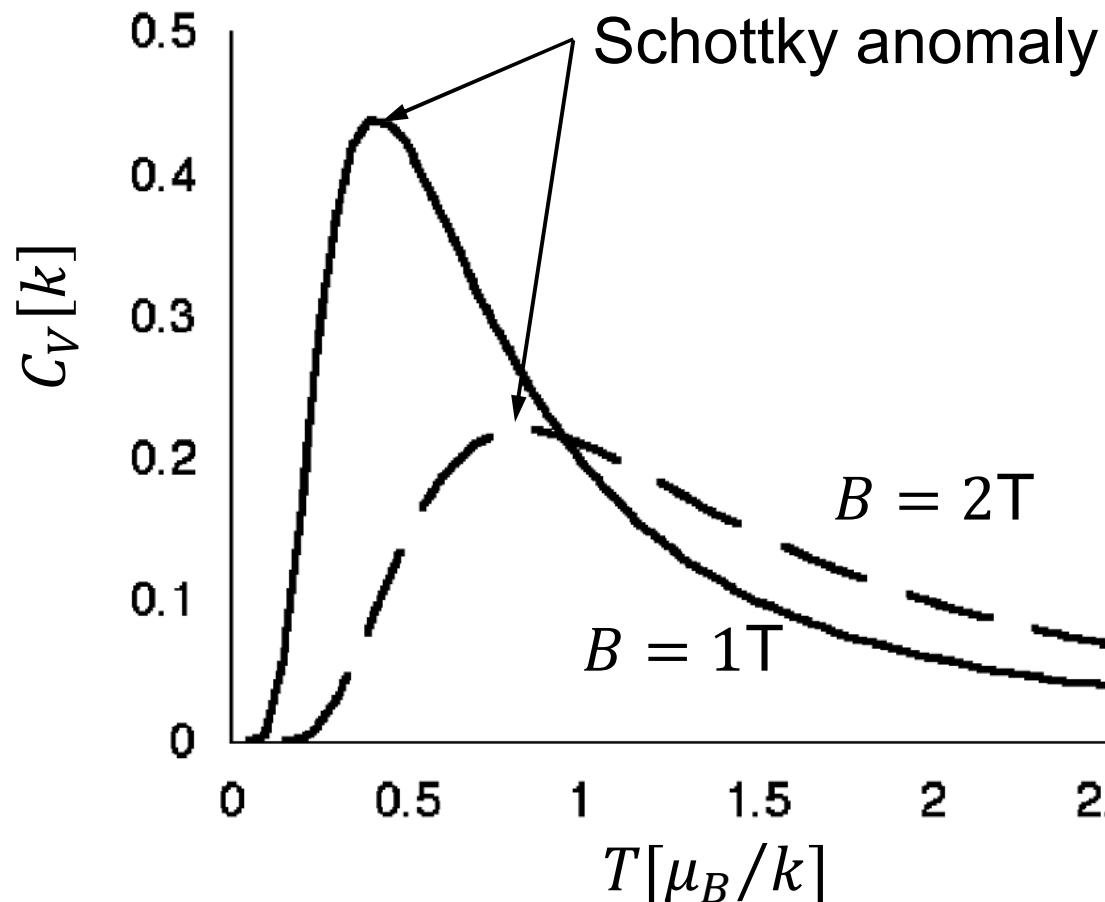
Thermodynamics determines defect concentrations and phase transformations, and influences magnetic properties, surface reactions, and crystal growth (the latter two are controlled by *kinetics*)

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

Thermodynamics

□ Example: Spins

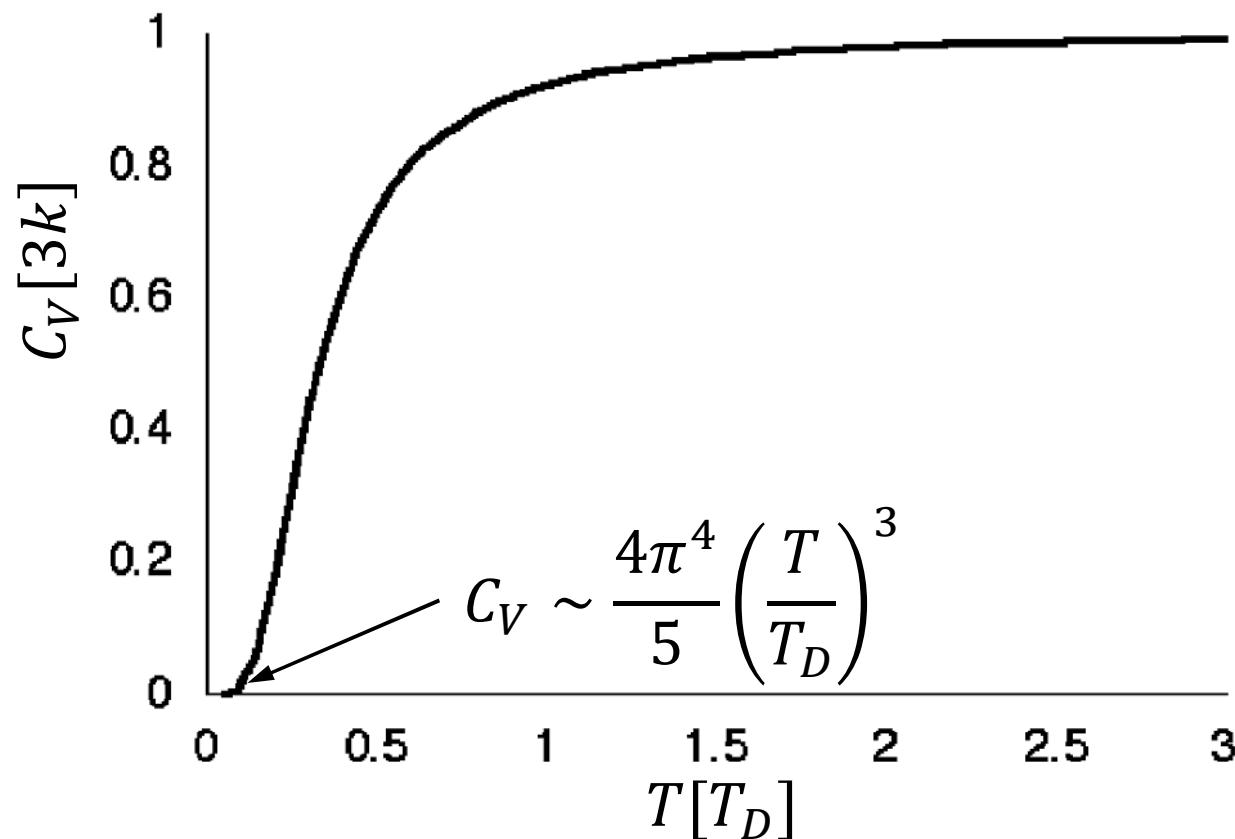
Heat capacity of a paramagnet



Thermodynamics

□ Example: Phonons

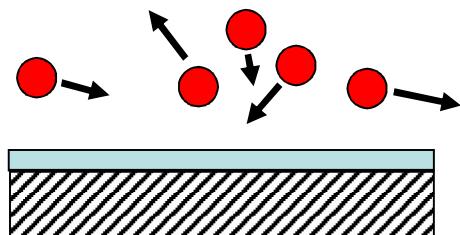
Heat capacity of a solid (Debye model - phonons in a box)



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

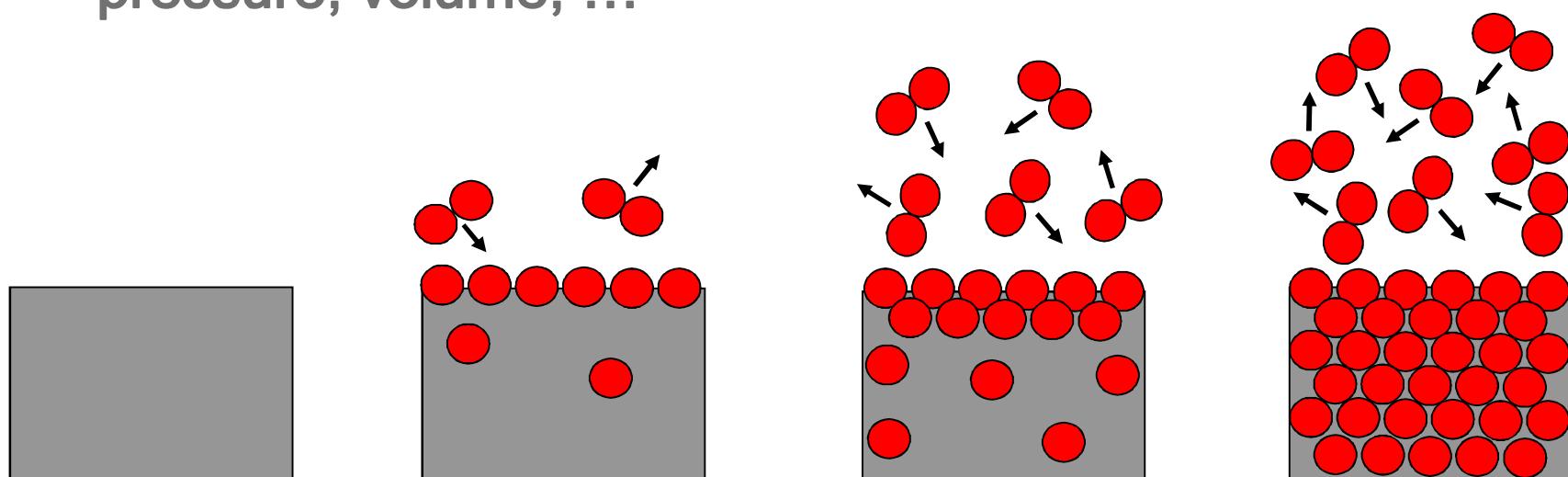
Adsorption will take place until the equilibrium is reached

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

Grand potential $\Omega(T, p, \{\mu\}) = U - TS - \sum_i N_i \mu_i$

Gibbs free energy 2 $G(T, p, \{N_{i \neq j}\}, \mu_j) = G - N_j \mu_j$

Energy balance equation

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

with chemical potentials

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

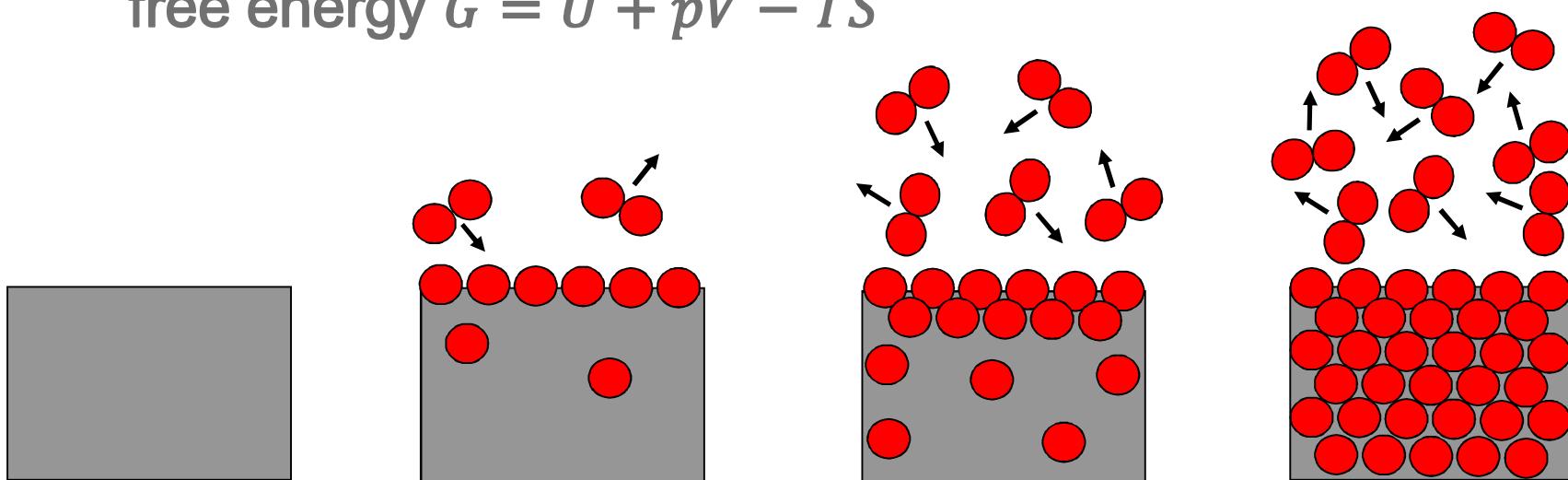
Thermodynamics

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 $W \rightarrow \text{max}$, 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: $\tilde{U} = \frac{N}{Z} \sum_i E_i e^{-E_i/kT} = \frac{NkT^2}{Z} \frac{\partial Z}{\partial T}$

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

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

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

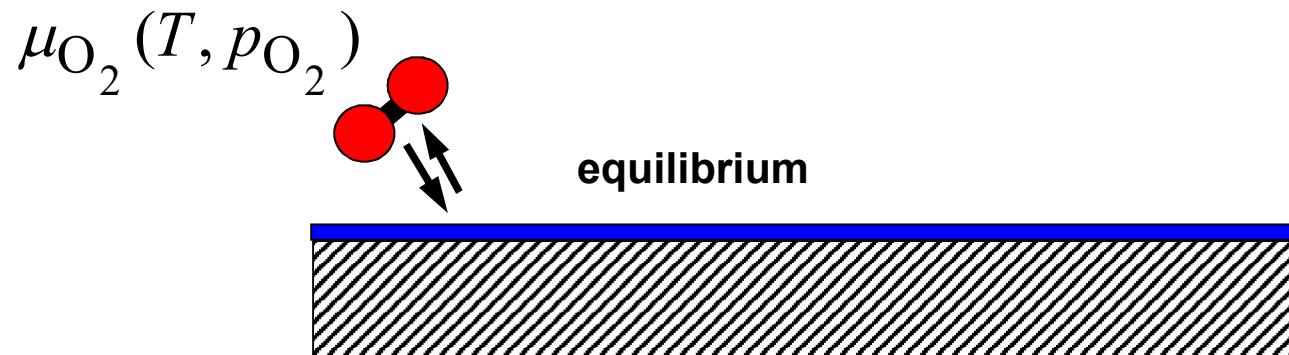
$$G = F + pV = -kT \ln Z + pV$$

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

Thermodynamics

□ Statistical thermodynamics

Practical example: surface free energy



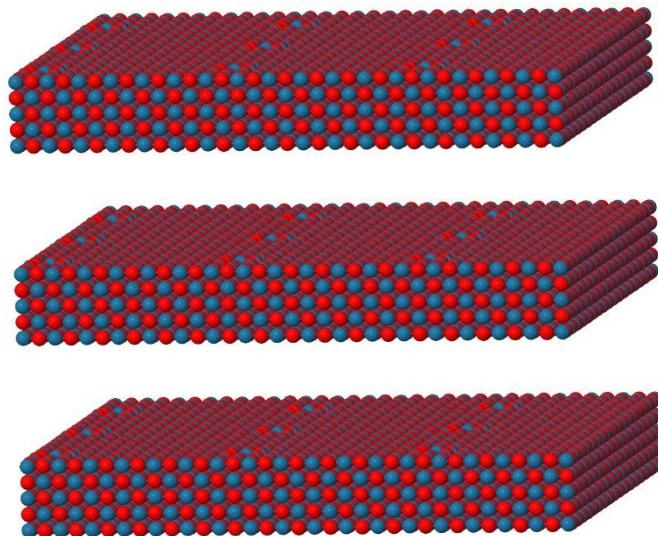
Change in Gibbs free energy upon addition of O to the surface: $\Delta G = G_{surf}(N_O + 1) - \left(G_{surf}(N_O) + \frac{1}{2} \mu_{O_2} \right)$

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

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

Surface modeling

1) Slab model (supercell approach)

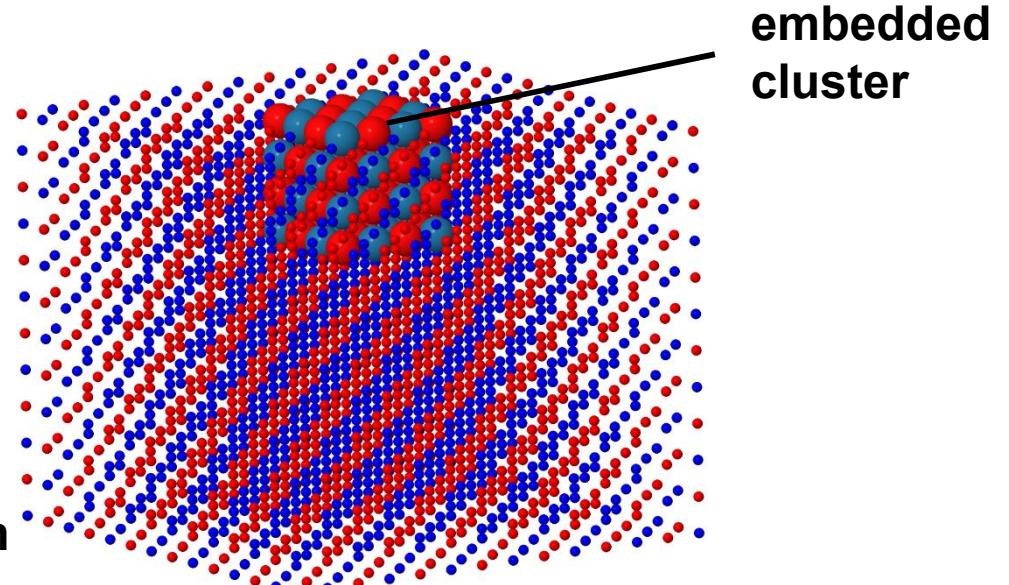


- + regular surfaces
- + coverage dependence
- ± defect-defect or adsorbate-adsorbate interaction

2) Cluster model:

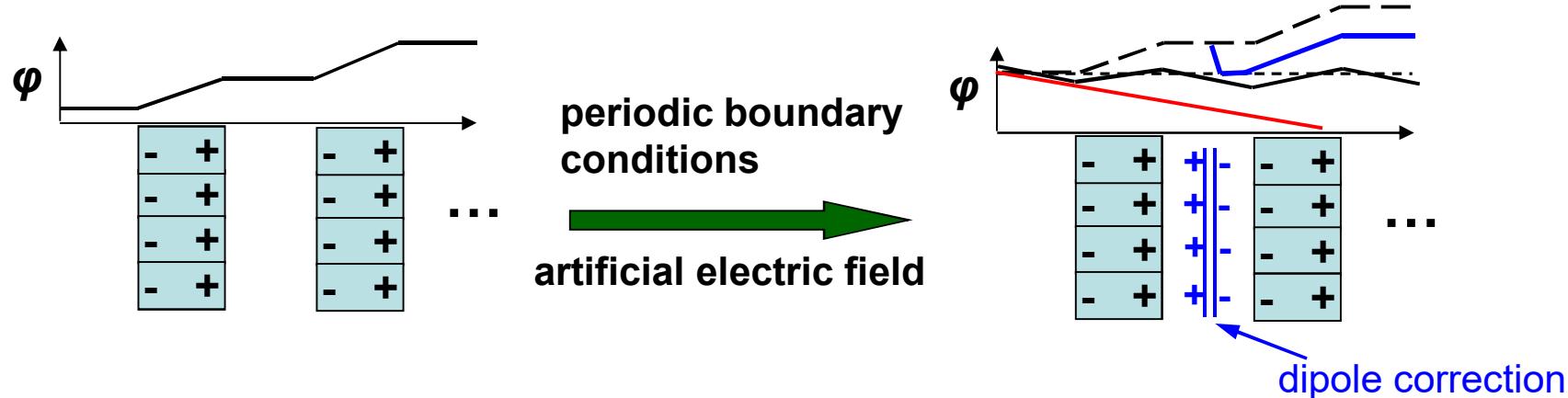
- + isolated defects or adsorbates
- border effects

Embedding: point charges (ionic systems), dangling bond saturation (covalently-bound systems),...

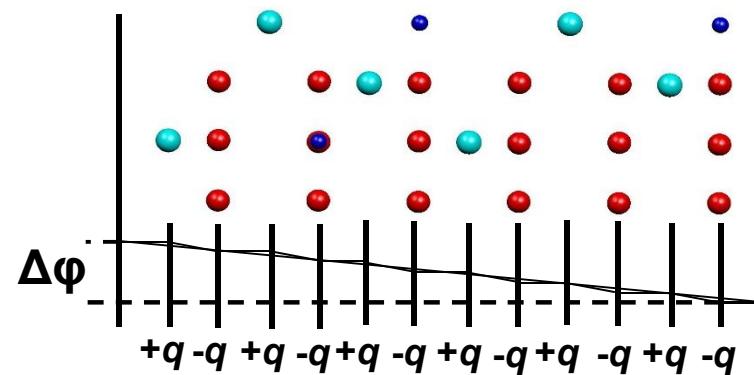
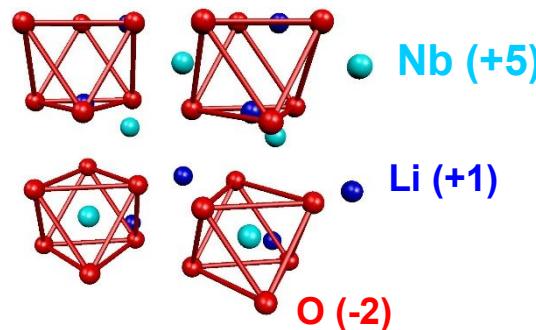


Surface modeling: important issues

- 1) Finite slab thickness (surface-surface interaction)
- 2) Finite vacuum layer thickness (image-image interactions)
- 3) Long-range interactions (charge, dipole moment)



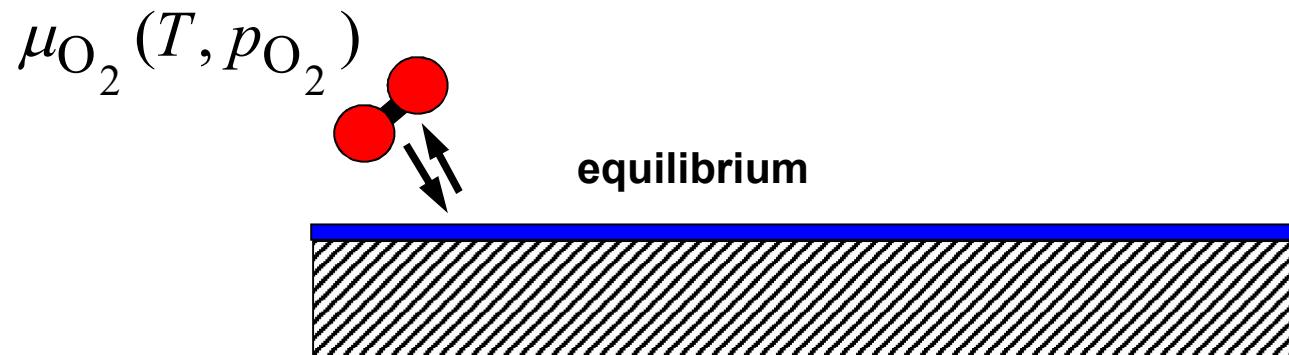
4) Surface polarity



Thermodynamics

□ Statistical thermodynamics

Practical example: surface free energy



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

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

Goal - find surface composition 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

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

$\mu_O(T, p)$ - ?

In thermodynamic equilibrium, μ is the same everywhere (gas, surface, bulk) - can calculate μ in gas

Thermodynamics

Statistical thermodynamics

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

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

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

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

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

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

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

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

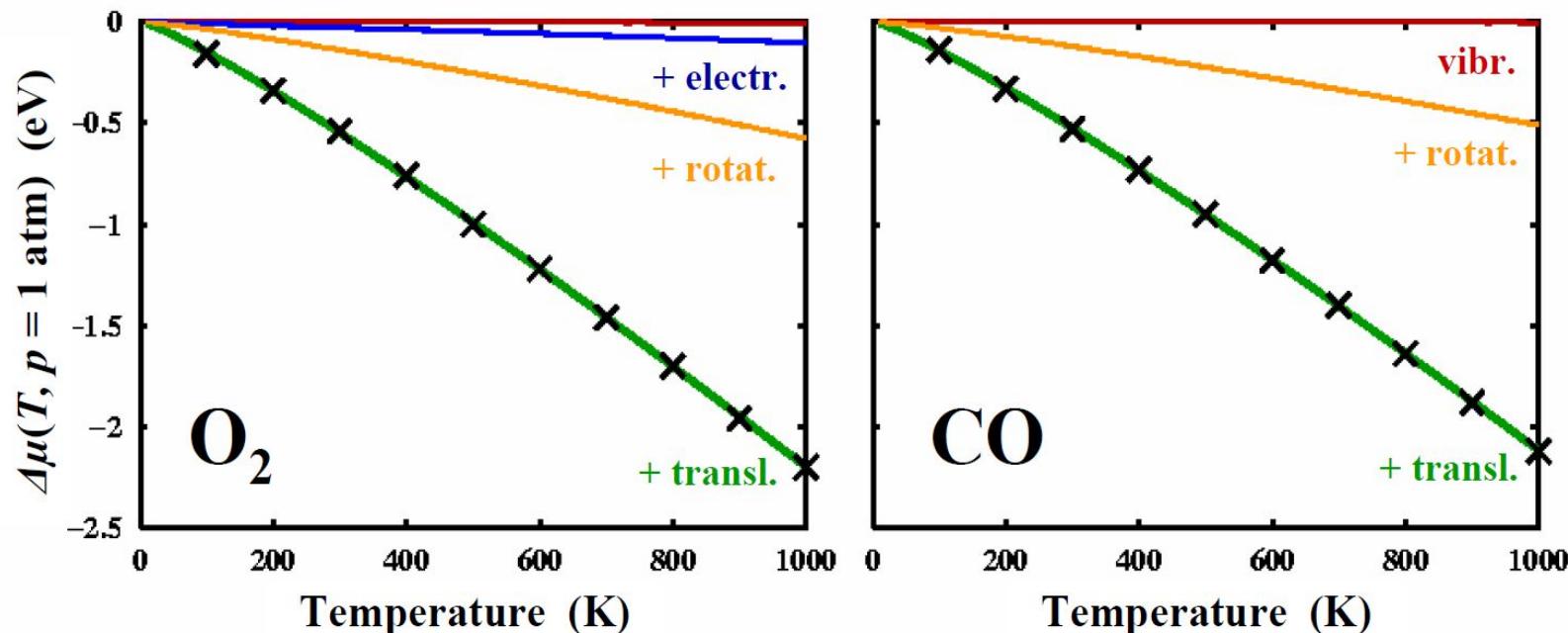
For a diatomic molecule $\mu_{vib} = \frac{\hbar\omega}{2} + kT \ln(1 - e^{-\hbar\omega/kT})$
required input - vibrational frequency ω

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 $\mu(T, p)$: $\mu(T, p) = E_0 + \Delta\mu(T, p)$

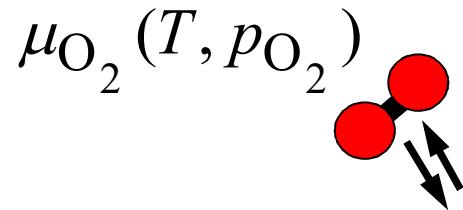


Alternatively: $\Delta\mu(T, p) = \Delta\mu(T, p^0) + k_B T \ln(p / p^0)$

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

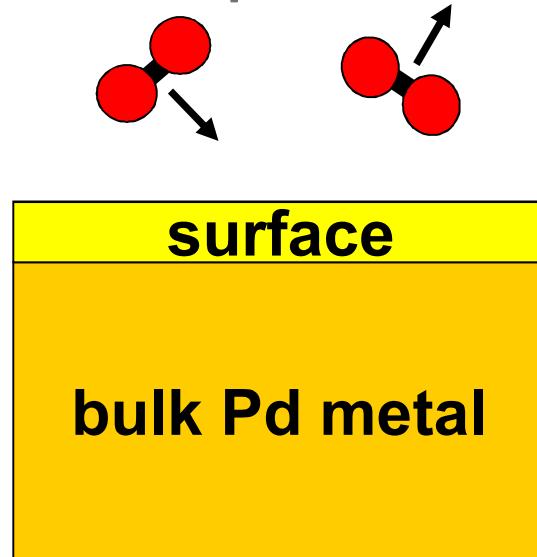
$$\Delta F_{vib}(T, V) = V \int_0^{\infty} f(T, \omega) (\sigma(\omega) - \sigma_{ref}(\omega)) d\omega, \quad \sigma(\omega) -$$

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



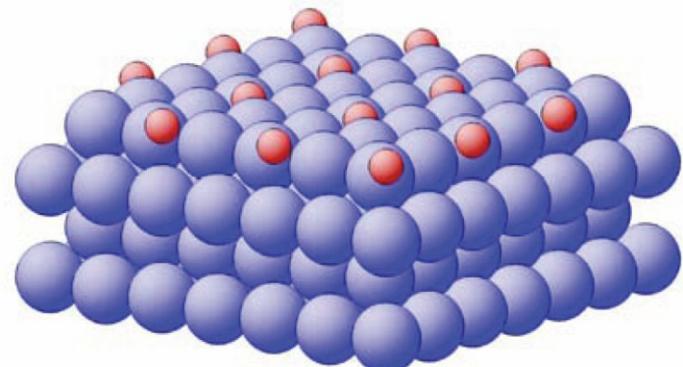
Reservoir: $\mu_O(T, p_{O_2})$ from ideal gas, $N_O^{ref} = 0$ (bare metal surface is the reference system), $\frac{1}{2}E_{O_2}$ is the reference for the chemical potential of O: $\mu_O = \Delta\mu_O + \frac{1}{2}E_{O_2}$

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

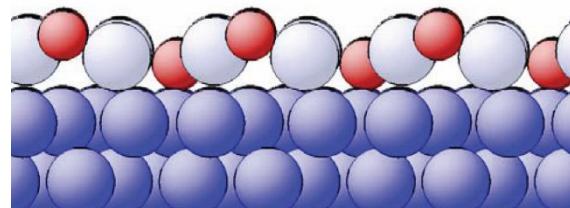
$$\Delta\gamma(T, p_{O_2}) = \frac{1}{A} \left[E_{surf}(N_O) - E_{surf}(0) - N_O \frac{1}{2}E_{O_2} \right] - \frac{1}{A} N_O \Delta\mu_O(T, p_{O_2})$$

Example: Pd(100)

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

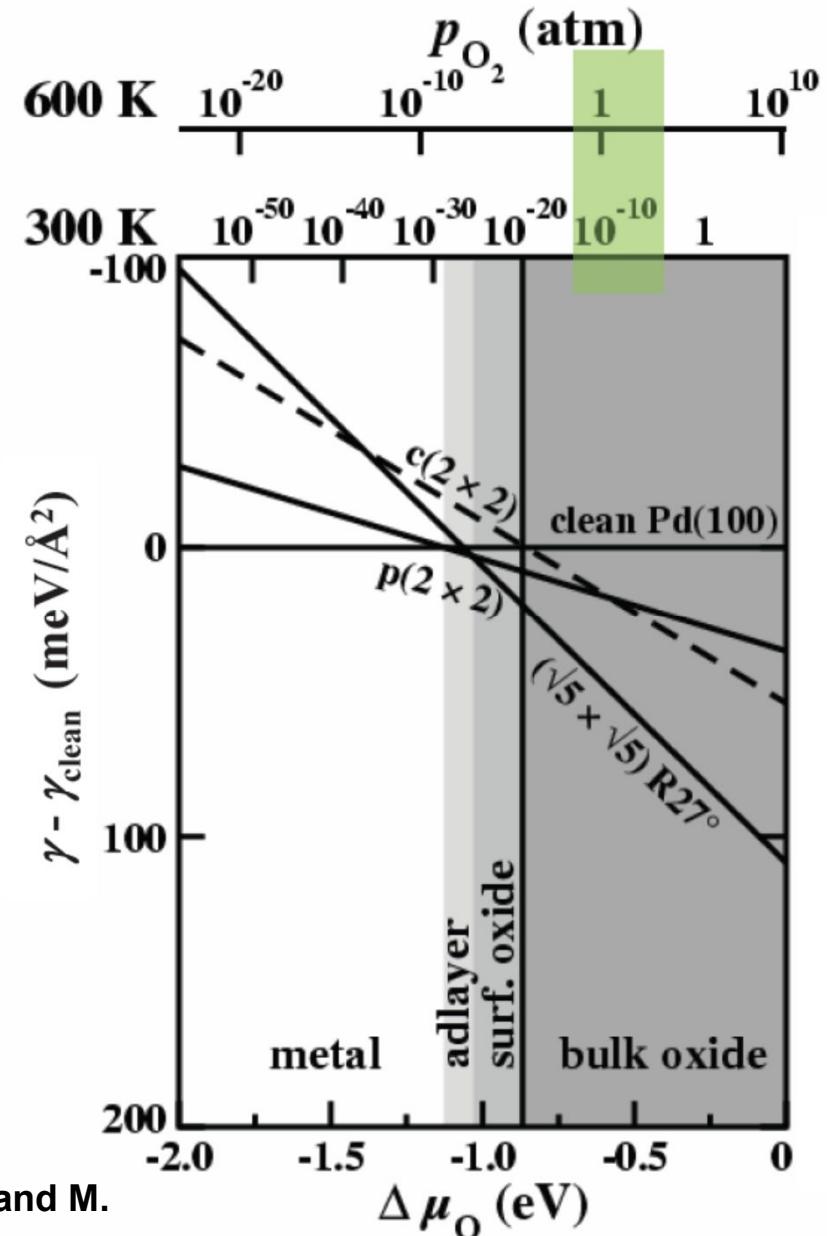


p(2x2) O/Pd(100)



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

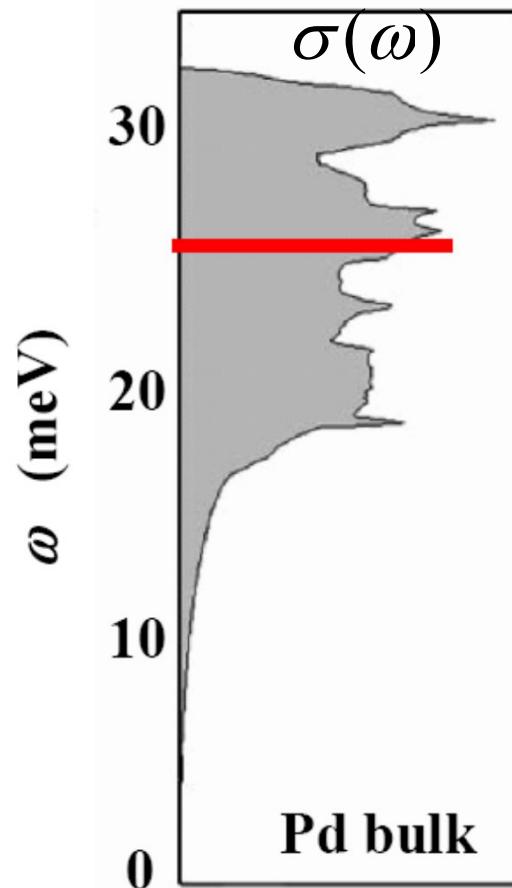
M. Todorova et al., Surf. Sci. 541, 101 (2003); K. Reuter and M. Scheffler, Appl. Phys. A 78, 793 (2004)



Thermodynamics

□ *Ab initio* atomistic thermodynamics

Vibrational contributions to the surface free energy:



$$\Delta F_{vib}(T, V) = V \int_0^{\infty} f(T, \omega) (\sigma(\omega) - \sigma_{ref}(\omega)) d\omega, \quad \sigma(\omega) - \text{phonon density of states}, \quad f(T, \omega) = \frac{\hbar\omega}{2} + kT \ln(1 - e^{-\hbar\omega/kT})$$

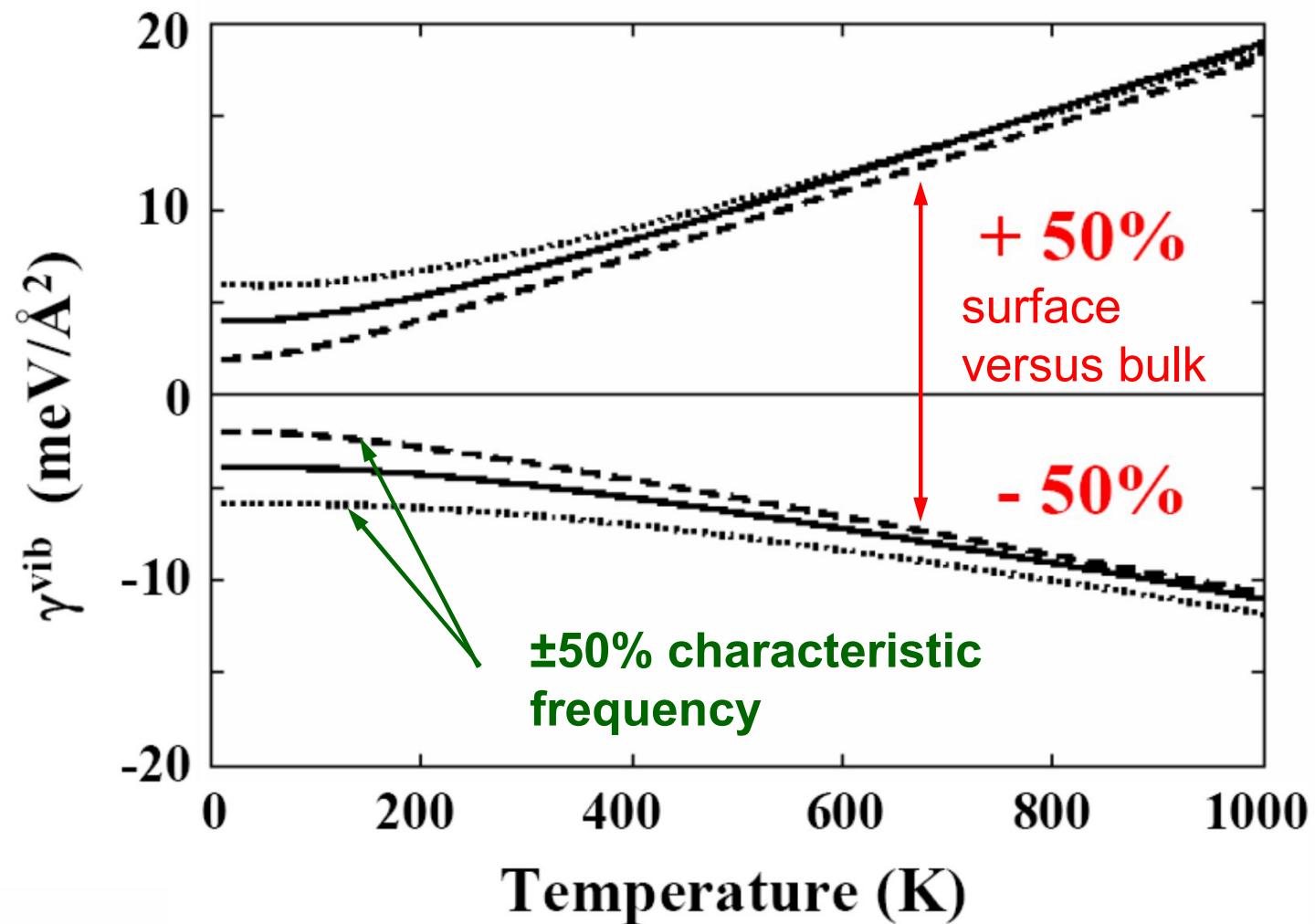
Only changes in vibrational free energy contribute to the surface free energy

Make estimate from simple models

e.g., Einstein model: $\sigma(\omega) = \delta(\omega - \langle \omega \rangle)$

$$\langle \omega \rangle_{\text{Pd}}(\text{bulk}) \sim 25 \text{ meV}$$

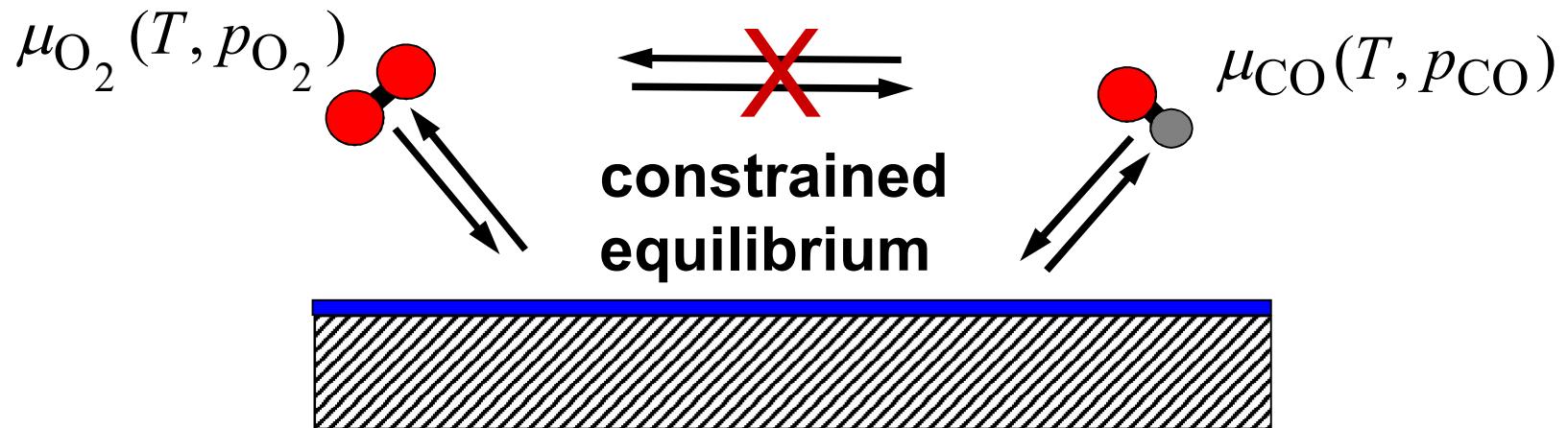
Surface-induced variations of substrate modes



< 10 meV/Å² for T = 600 K – in this case!!!

K. Reuter and M. Scheffler, Phys. Rev. B 65, 035406 (2001)

First-principles atomistic thermodynamics: constrained equilibria

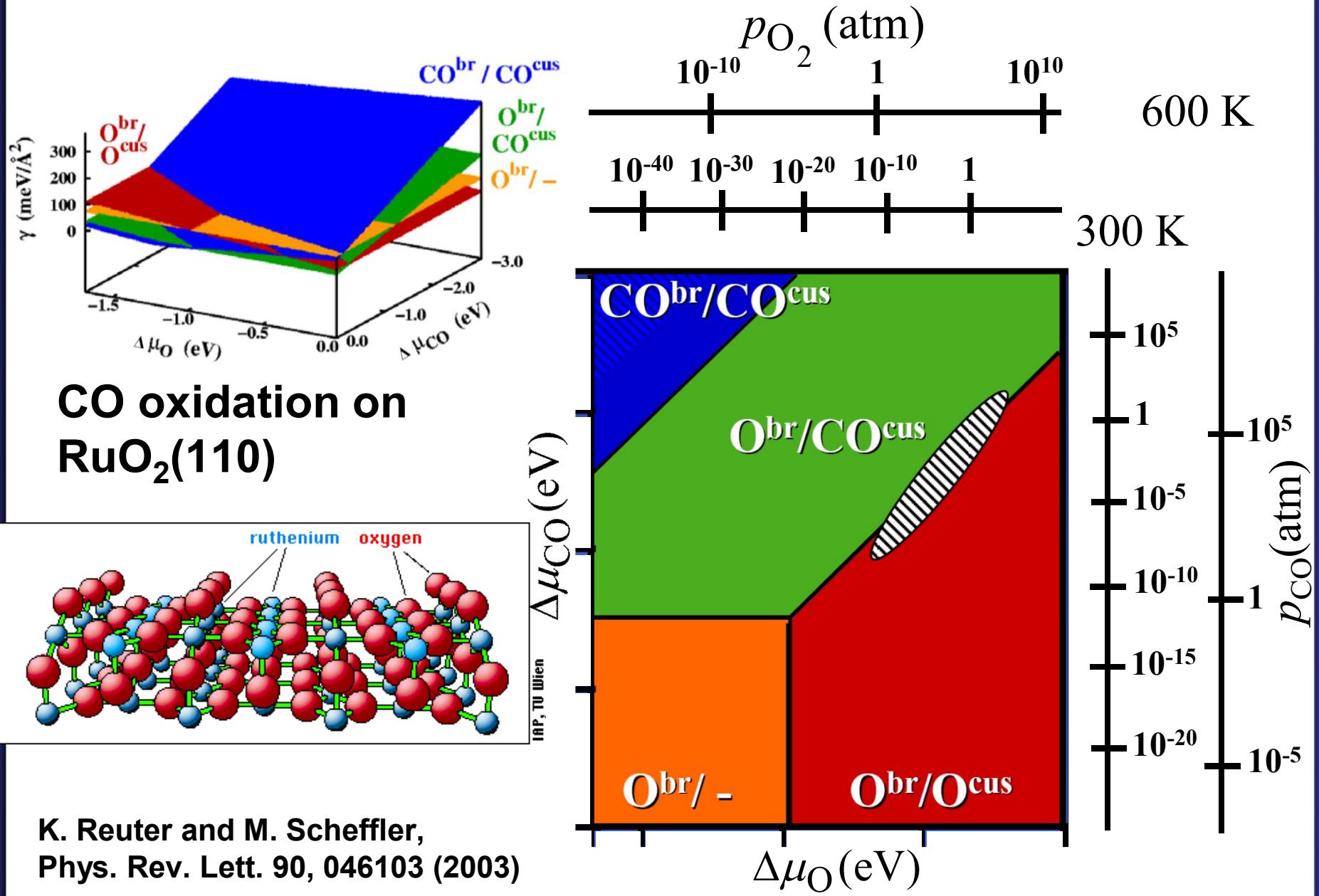


$$\Delta\gamma(T, p_{O_2}) = \frac{1}{A} \left[E_{surf}(N_O, N_{CO}) - E_{surf}^{ref} - N_O \frac{1}{2} E_{O_2} - N_{CO} E_{CO} \right]$$
$$- \frac{1}{A} N_O \Delta\mu_O(T, p_{O_2}) - \frac{1}{A} N_{CO} \Delta\mu_{CO}(T, p_{CO})$$

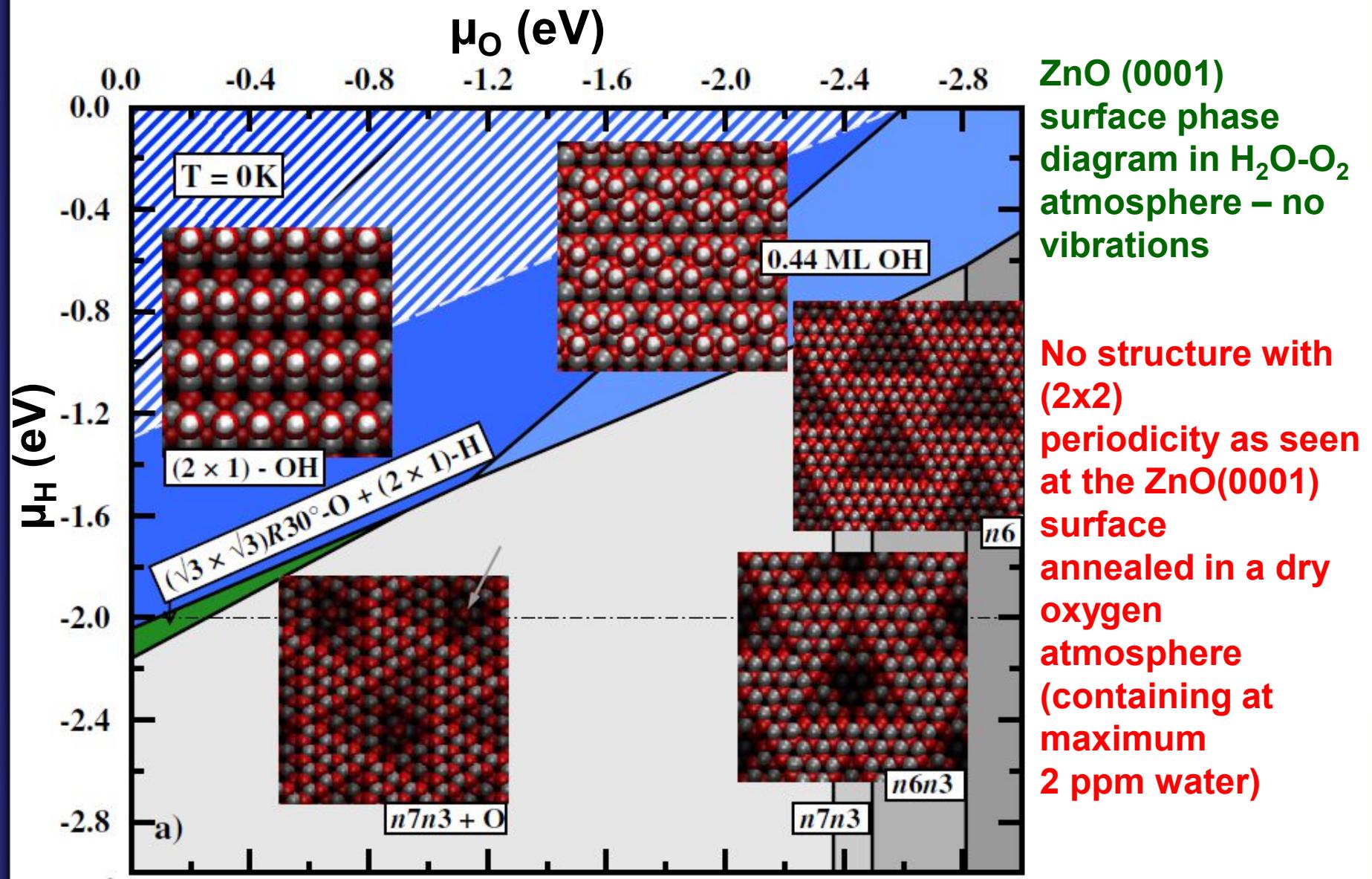
C.M. Weinert and M. Scheffler, Mater. Sci.
Forum 10-12, 25 (1986); E. Kaxiras *et al.*,
Phys. Rev. B 35, 9625 (1987);

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

Surface phase diagrams

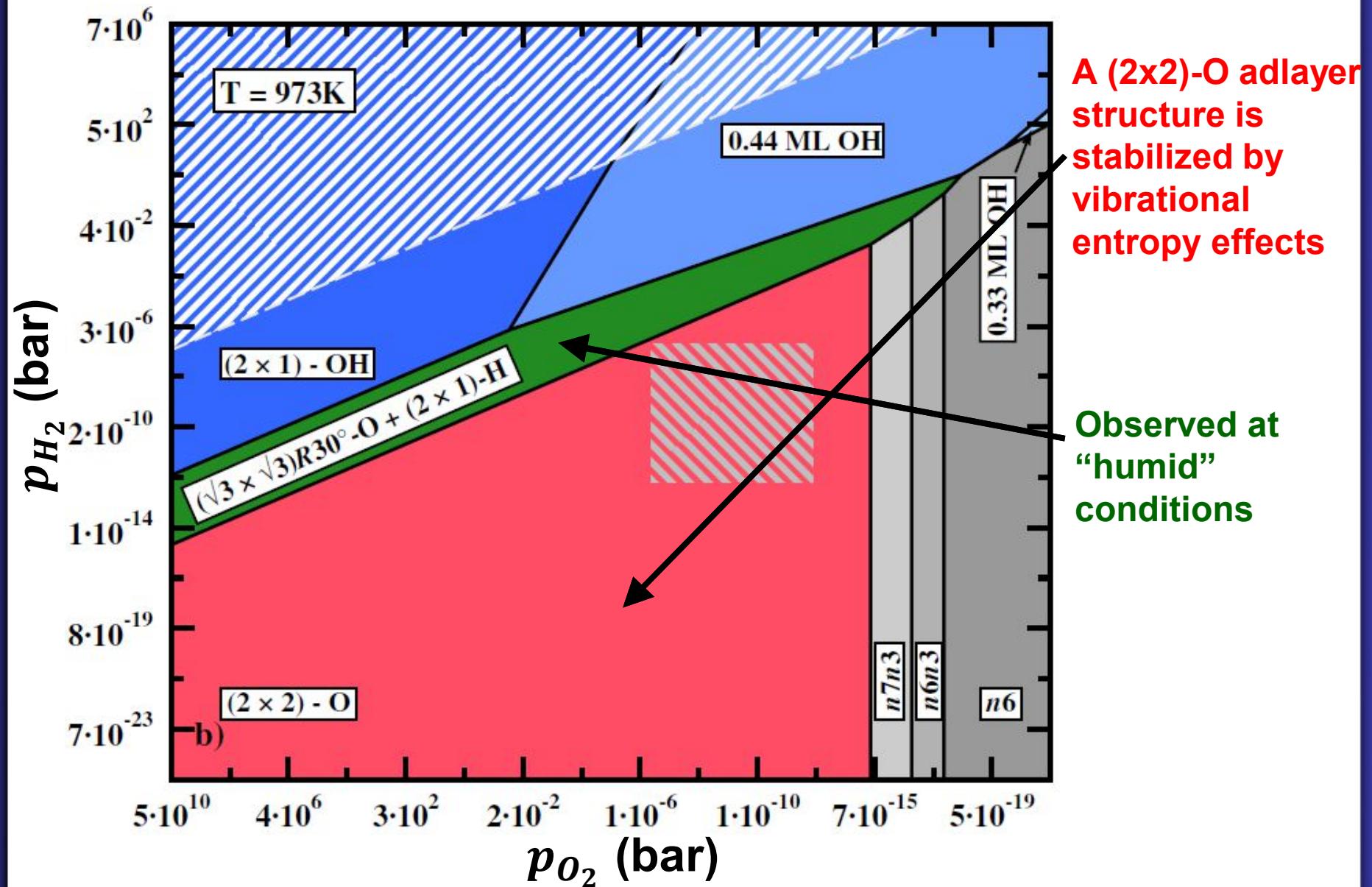


When vibrations do matter



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

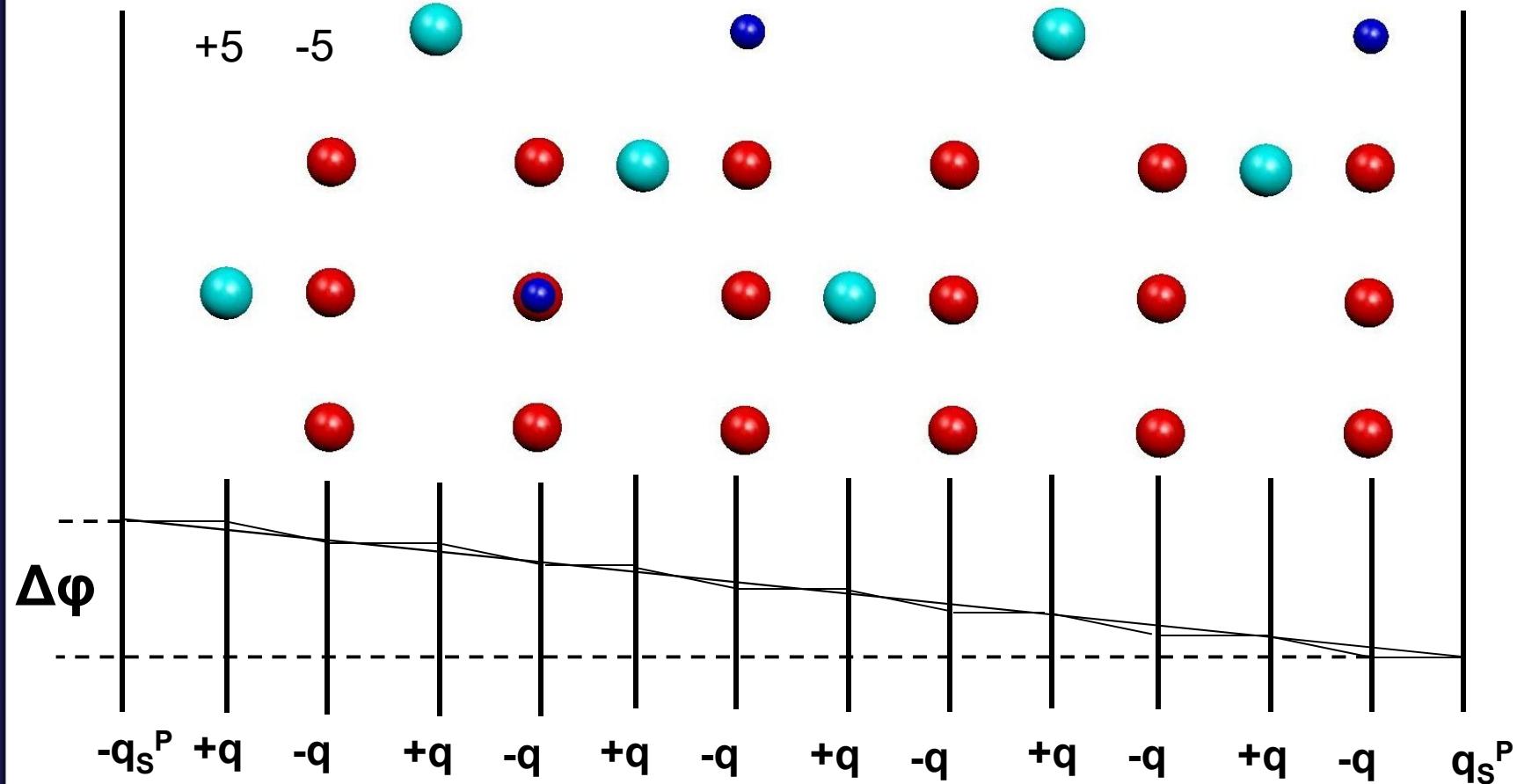
When vibrations do matter



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Polar surfaces

Paraelectric lithium niobate (LiNbO_3) stoichiometric surfaces:

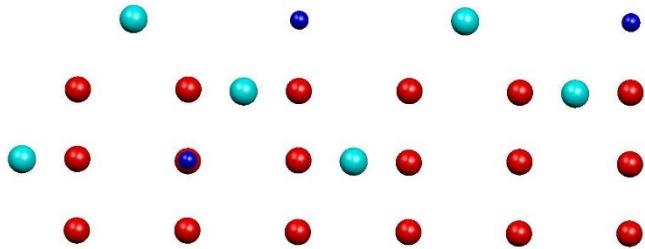


$$q_s^P = -q/2 \approx -2.5e \neq 0 - \text{surface charge}, P_{PE} \neq 0$$

$\Delta\phi \approx 250 \text{ V} \gg E_g/e \approx 3.7 \text{ V} \rightarrow \text{surface charge almost completely passivated}$

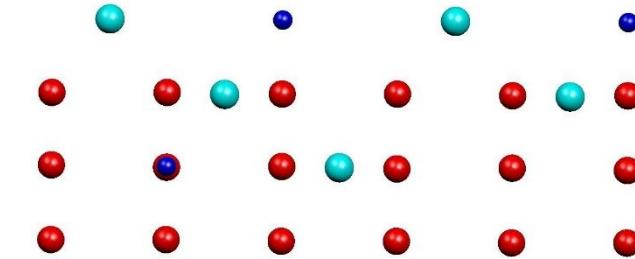
Polar surfaces

Where to cut?



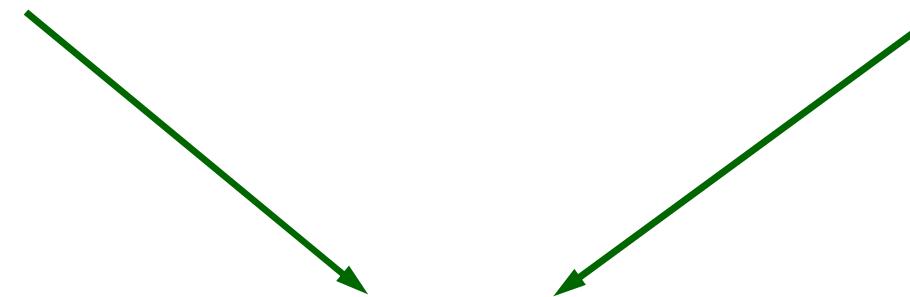
Charge = 0,

Dipole moment $\neq 0$



Charge = -5e,

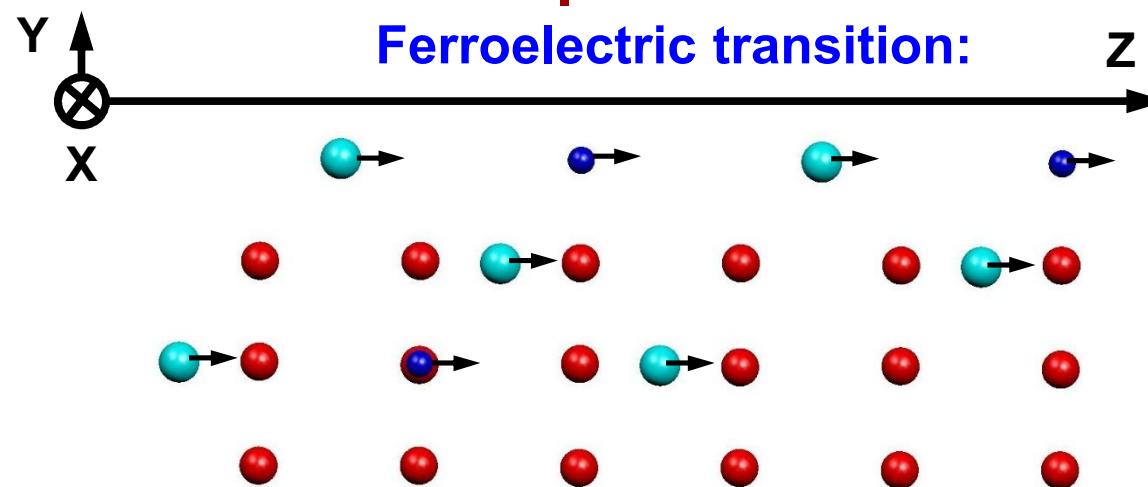
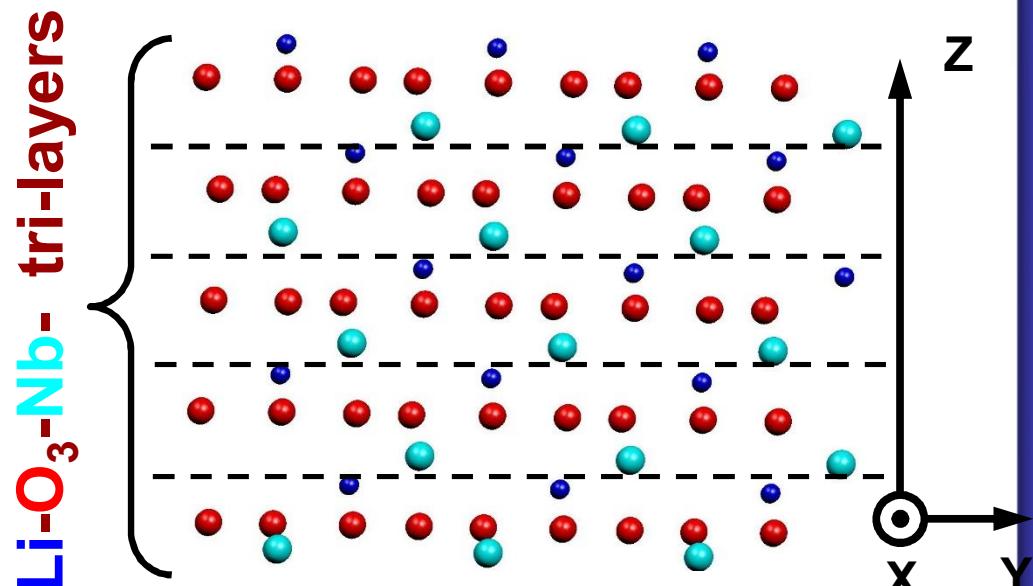
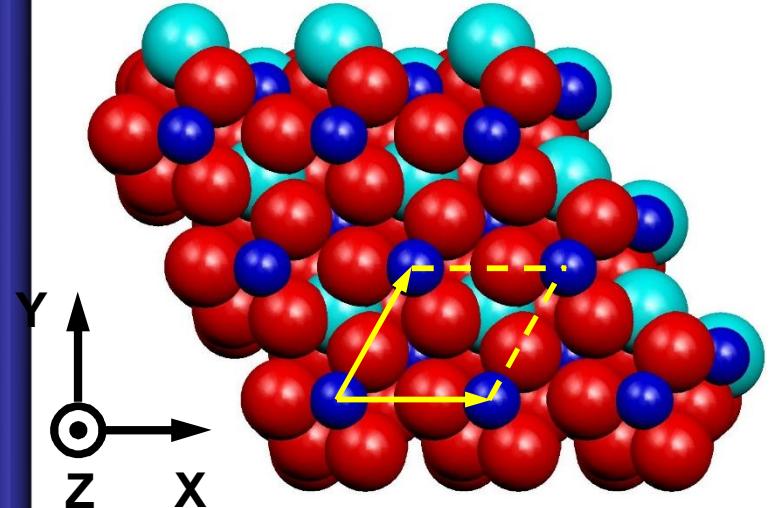
Dipole moment = 0



Surface charge = $\pm 2.5e$

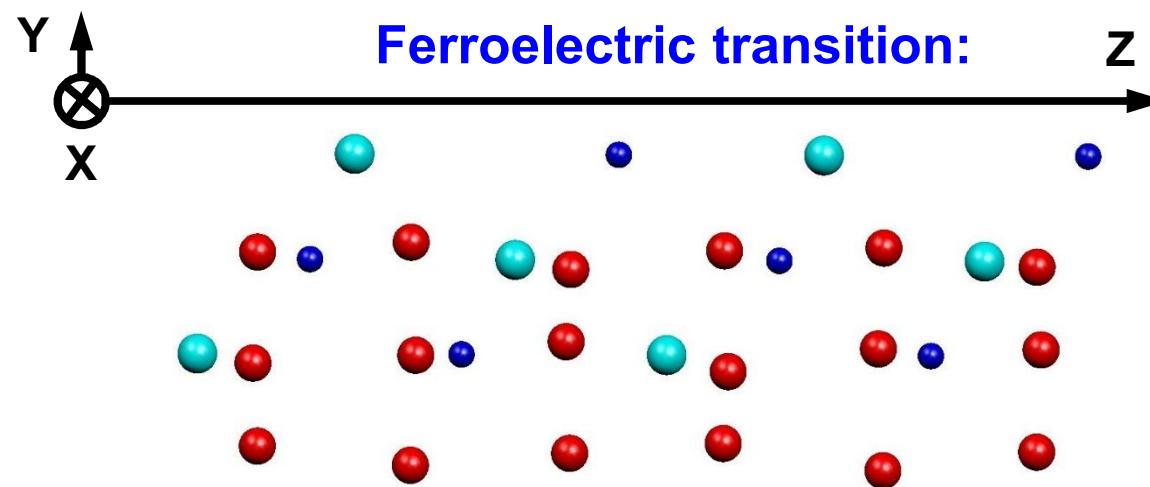
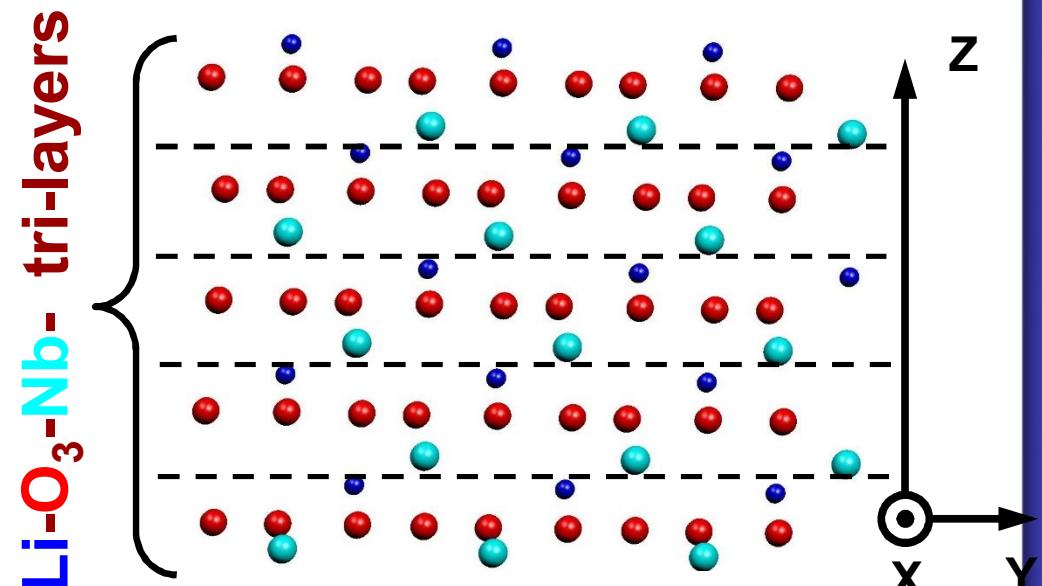
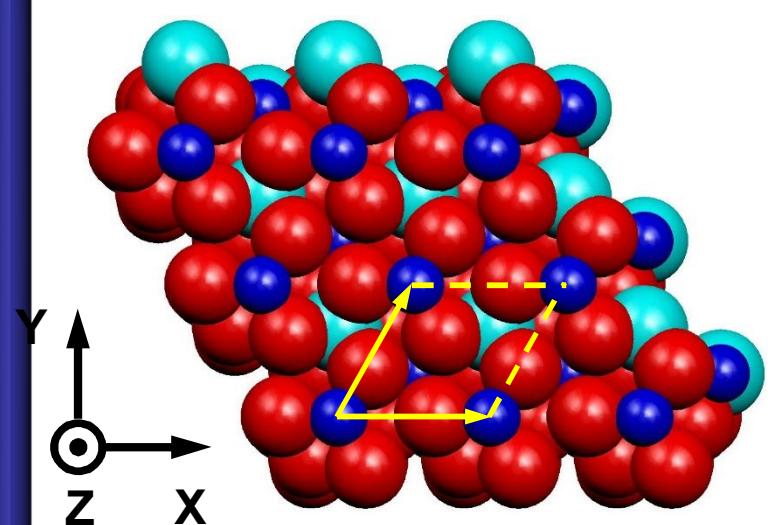
Ferroelectric lithium niobate LiNbO_3 .

Unrelaxed stoichiometric surface and layer stacking:

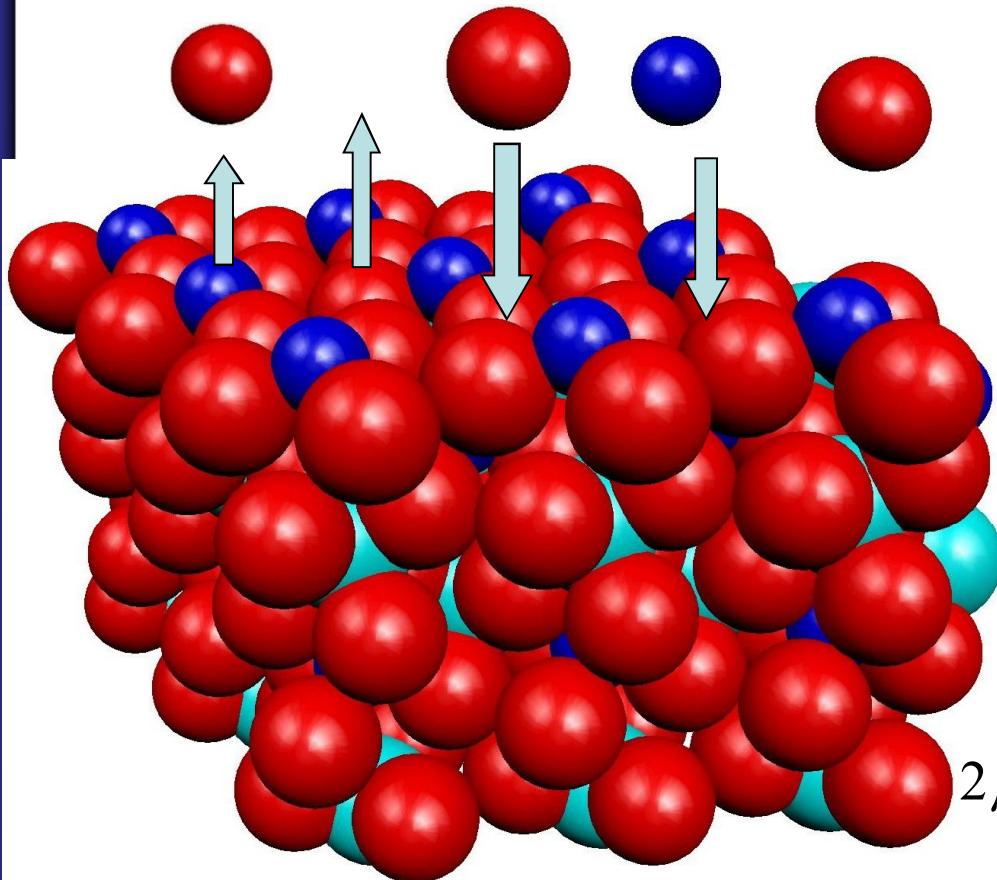


Ferroelectric lithium niobate LiNbO_3

Unrelaxed stoichiometric surface and layer stacking:



Surface and environment.



Chemical potentials μ_{Li} , μ_O , and μ_{Nb} such that:

1) bulk LN is stable:

$$\mu_{Li} + \mu_{Nb} + 3\mu_O = g_{LN}^{bulk}$$

2) no other condensed phases are stable:

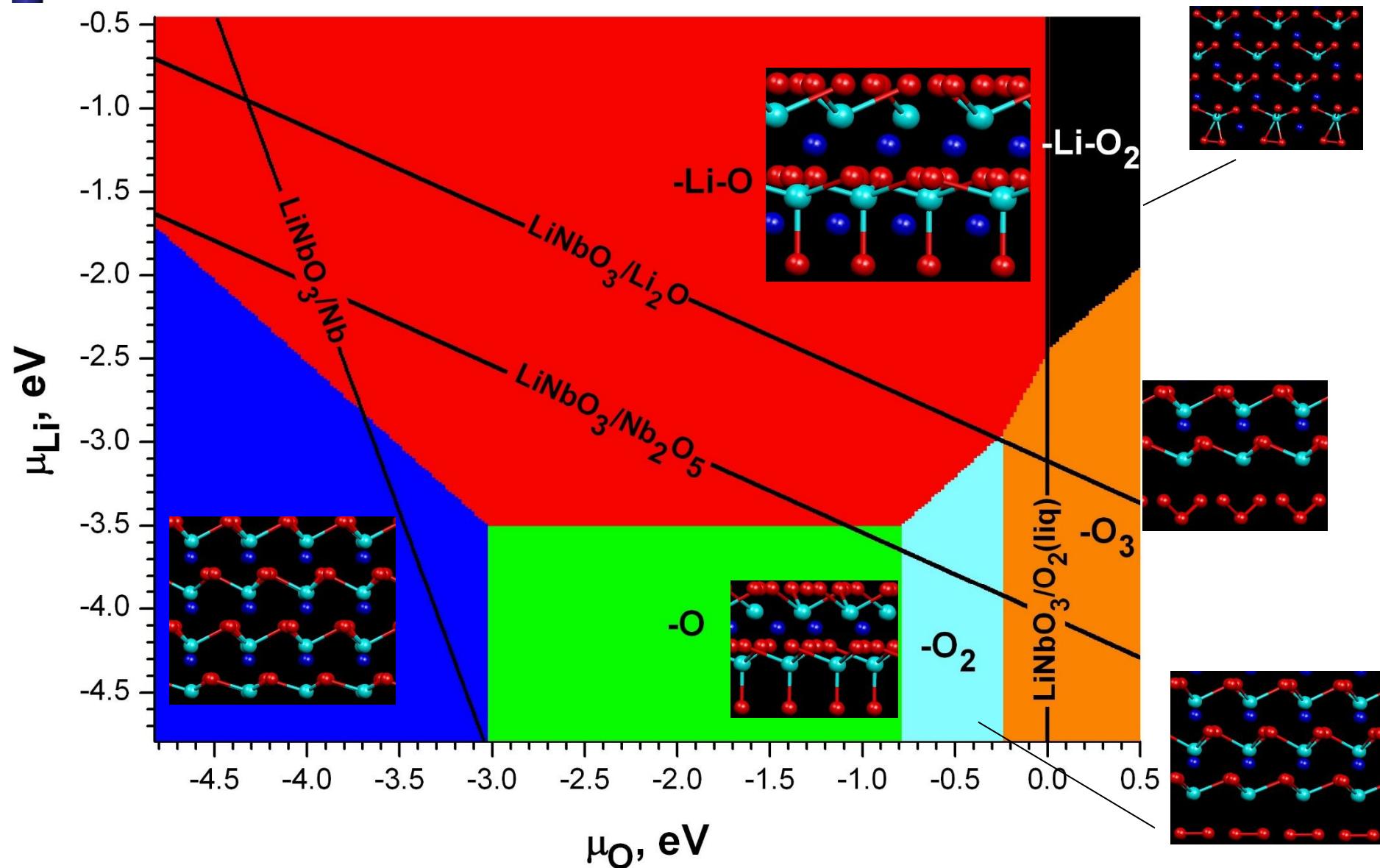
$$2\mu_{Li} + \mu_O < g_{Li_2O}^{bulk}, \quad 2\mu_{Nb} + 5\mu_O < g_{Nb_2O_5}^{bulk}$$

$$\mu_O < \mu_O^{\max} \approx \frac{1}{2} g_{O_2}, \quad \mu_{Li} < \mu_{Li}^{\max} \approx g_{Li}^{bulk}, \quad \mu_{Nb} < \mu_{Nb}^{\max} \approx g_{Nb}^{bulk}$$

Surface free energy:

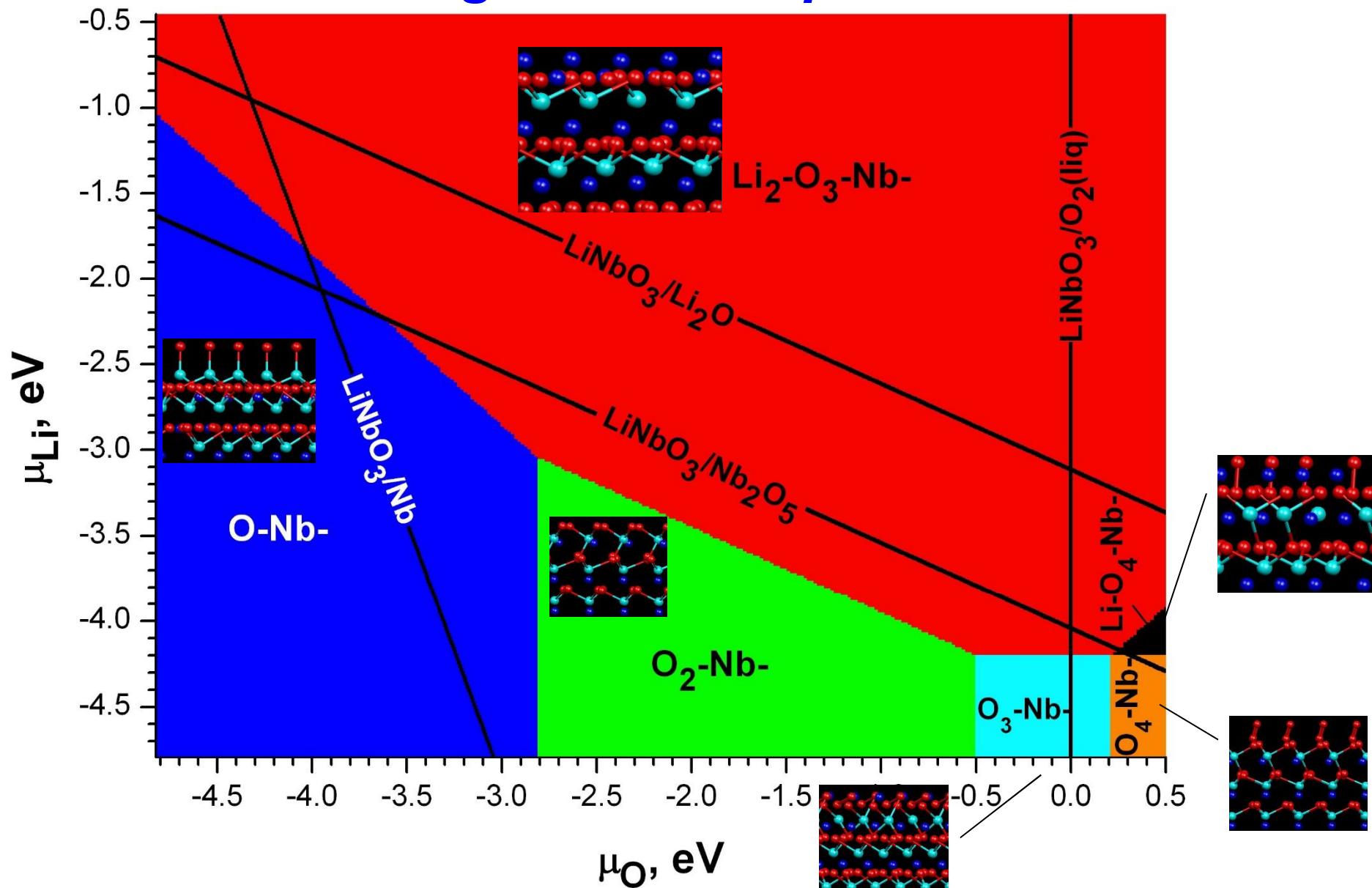
$$\gamma(T, p) = G^{slab}(N_{Nb}, N_{Li}, N_O) - \mu_{Nb}(T, p)N_{Nb} - \mu_{Li}(T, p)N_{Li} - \mu_O(T, p)N_O$$

Phase diagram for the *negative* surface



Levchenko, Rappe, PRL 100, 256101 (2008)

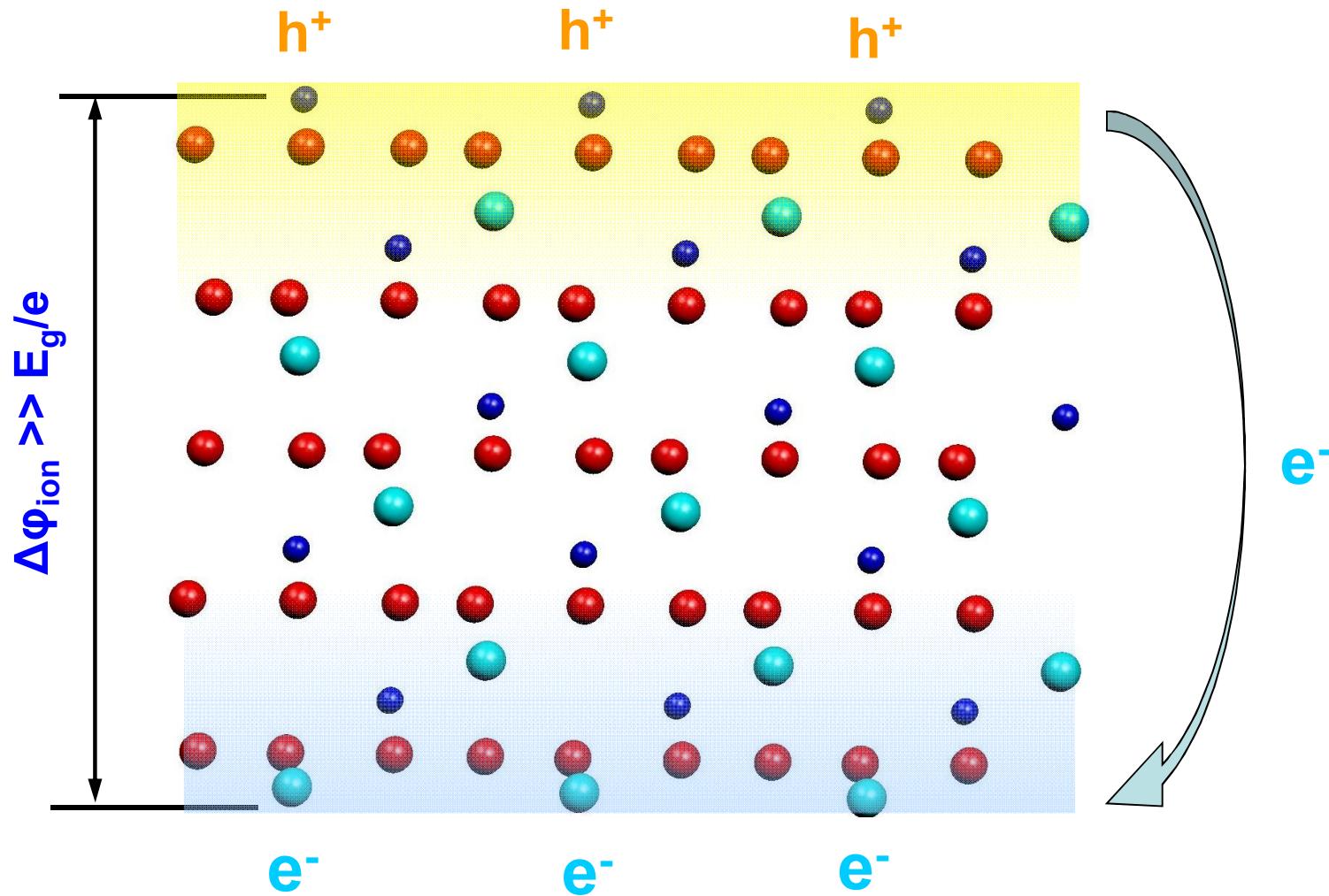
Phase diagram for the positive surface



Levchenko, Rappe, PRL 100, 256101 (2008)

Surface charge passivation

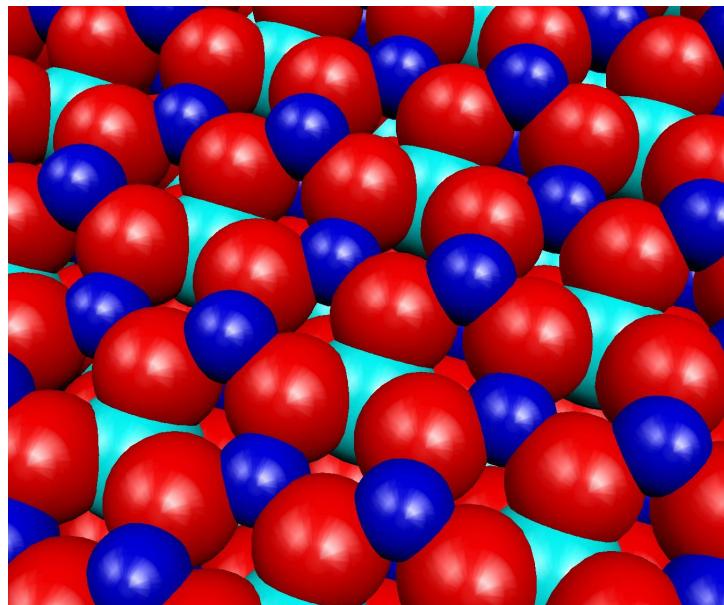
Fixed stoichiometry: surface charge passivated by electrons and holes.



About 1e/unit cell is transferred

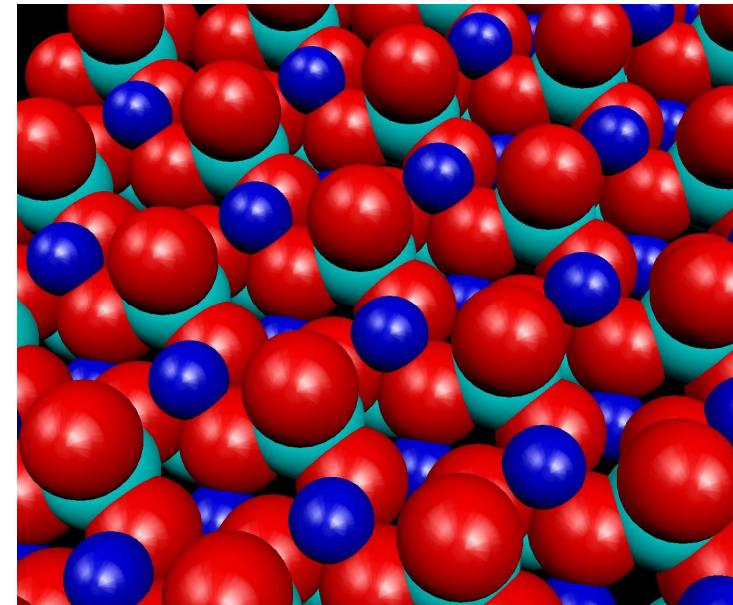
Most stable terminations: explanation

positive surface:



Accommodates compensating
 h^+ : additional Li stabilizes h^+
by forming Li^+

negative surface:



Accommodates compensating
 e^- : additional LiO stabilizes e^-
by forming LiO^-

Compensation with ions is preferred over compensation with mobile charges!

Levchenko, Rappe, PRL 100, 256101 (2008)