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

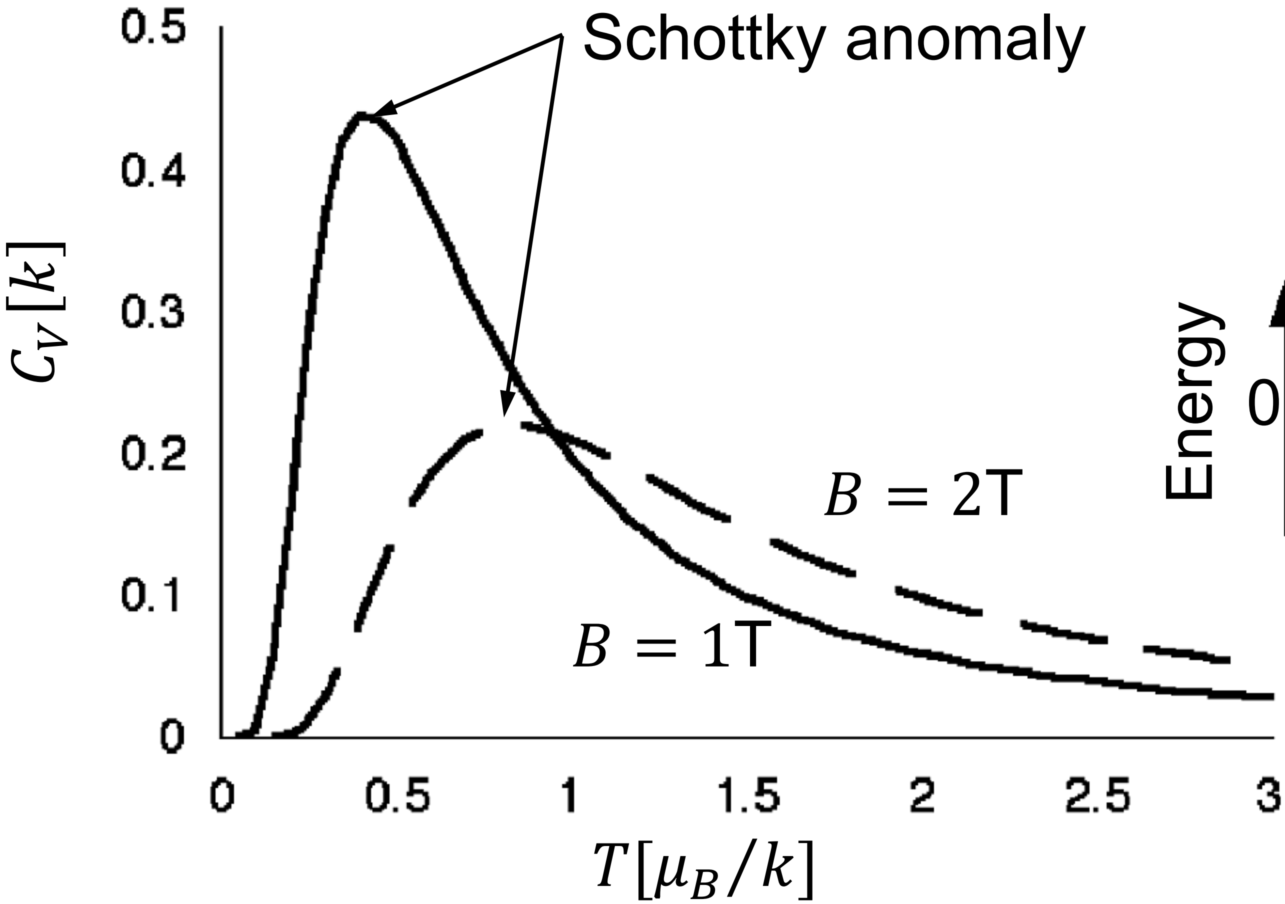
  Thermodynamics determines defect concentrations and phase transformations, and influences magnetic properties, surface reactions, and crystal growth (the latter two are controlled by *kinetics*)

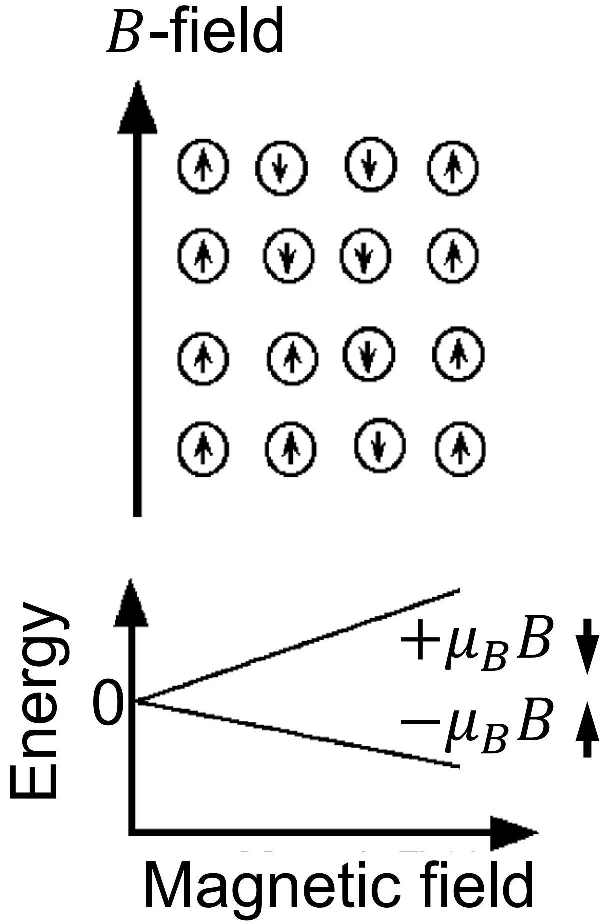
  There is always a particle exchange between the material and its environment at finite T

Thermodynamics

- **Example: Spins**

  Heat capacity of a paramagnet

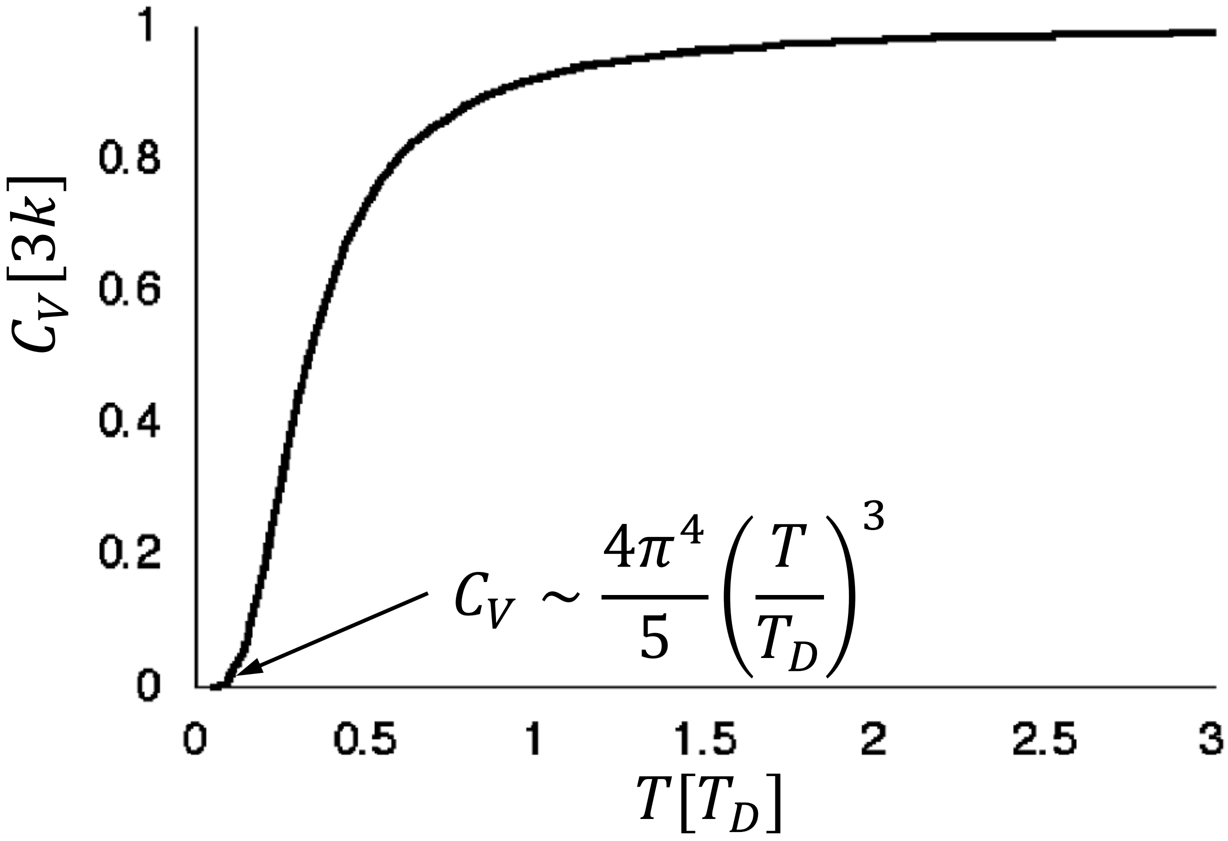




Thermodynamics

- **Example: Phonons**

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

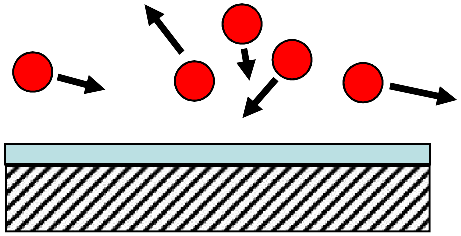


$$C_V \sim \frac{4\pi^4}{5}\left(\frac{T}{T_D}\right)^3$$

Thermodynamics

❐ Example

Consider a metal surface in an oxygen atmosphere



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

For T = 300 K, p = 1 atm → $\nu \sim 10^{8}$ site^{-1} s^{-1}

⇨

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

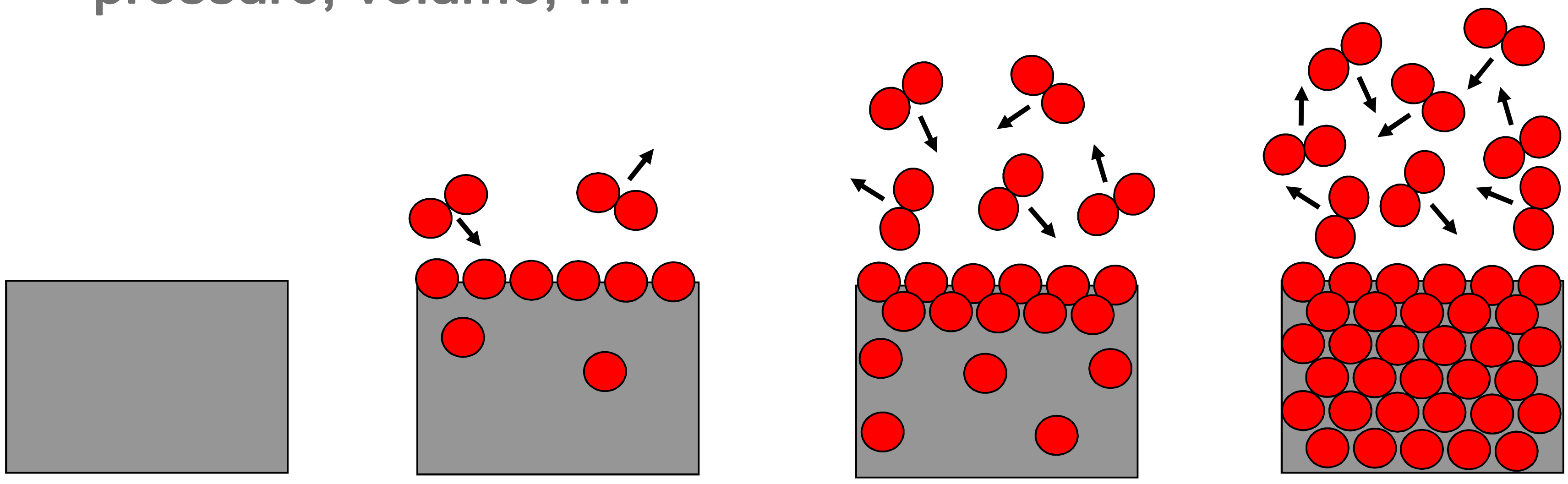
Adsorption will take place until the equilibrium is reached

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

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

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

Energy balance equation

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

with chemical potentials

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

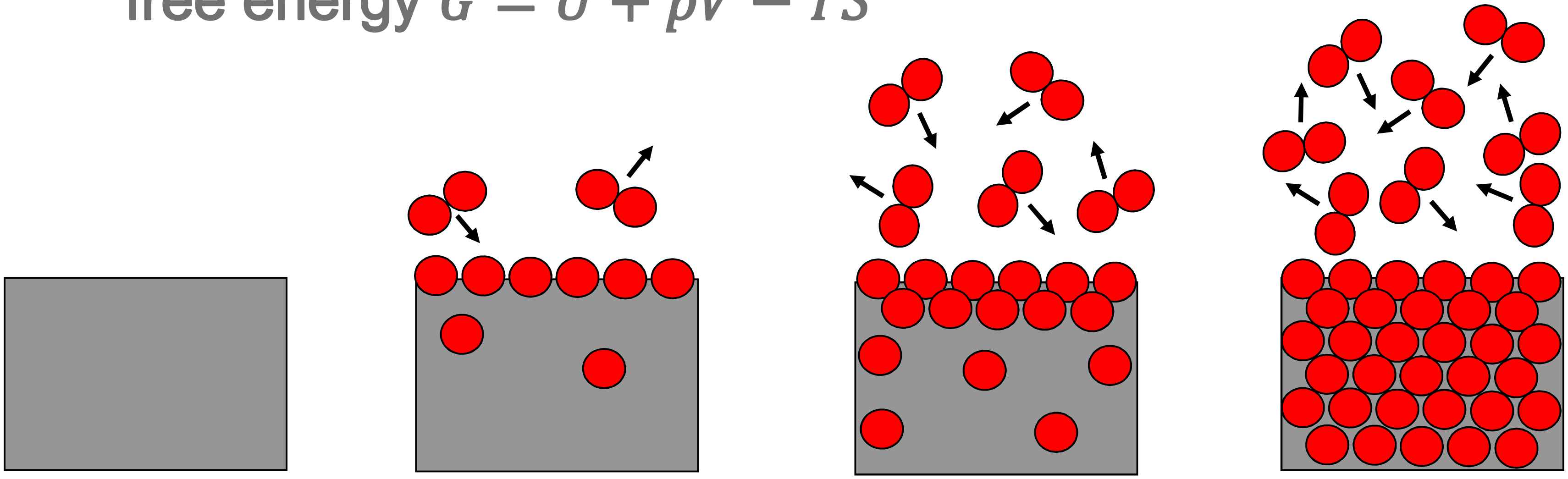
Thermodynamics

❒ 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 from probability laws 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,… 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: $\tilde{U} = \frac{N}{Z}\sum_i E_i e^{-E_i/kT} = \frac{NkT^2}{Z}\frac{\partial Z}{\partial T}$

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

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

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

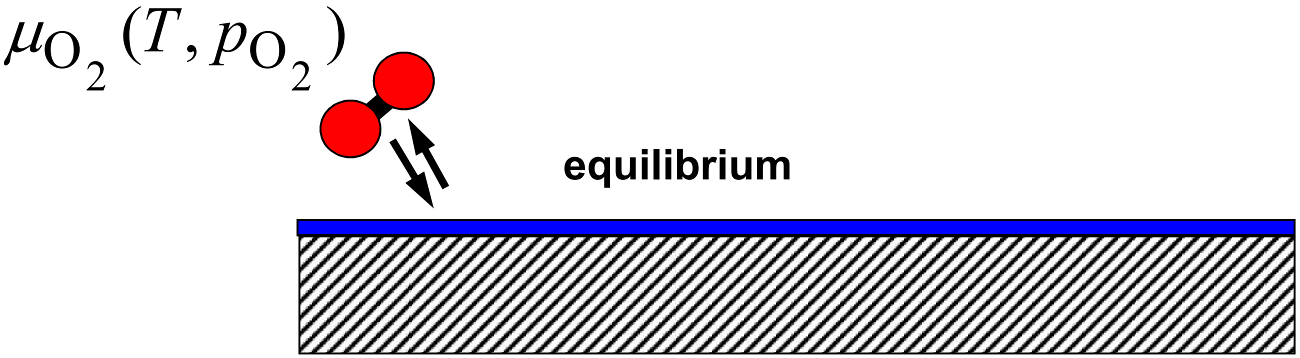
$$G = F + pV = -kT\ln Z + pV$$

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

Thermodynamics

❐ Statistical thermodynamics

Practical example: surface free energy



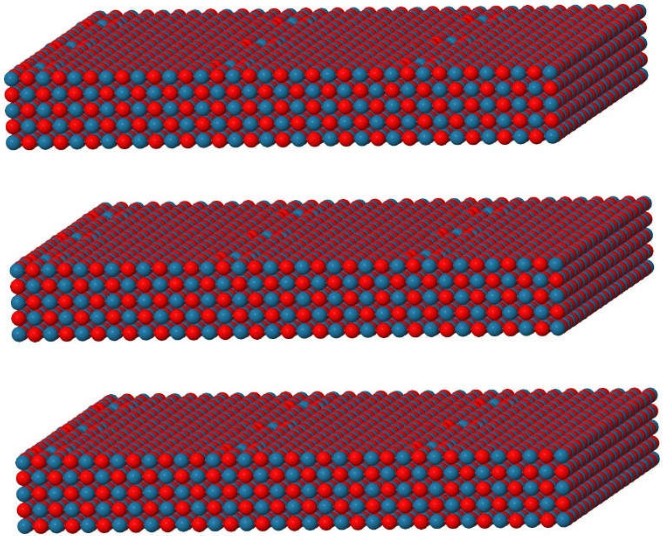
Change in Gibbs free energy upon addition of O to the surface: $\Delta G = G_{surf}(N_O + 1) - \left(G_{surf}(N_O) + \frac{1}{2}\mu_{O_2}\right)$

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

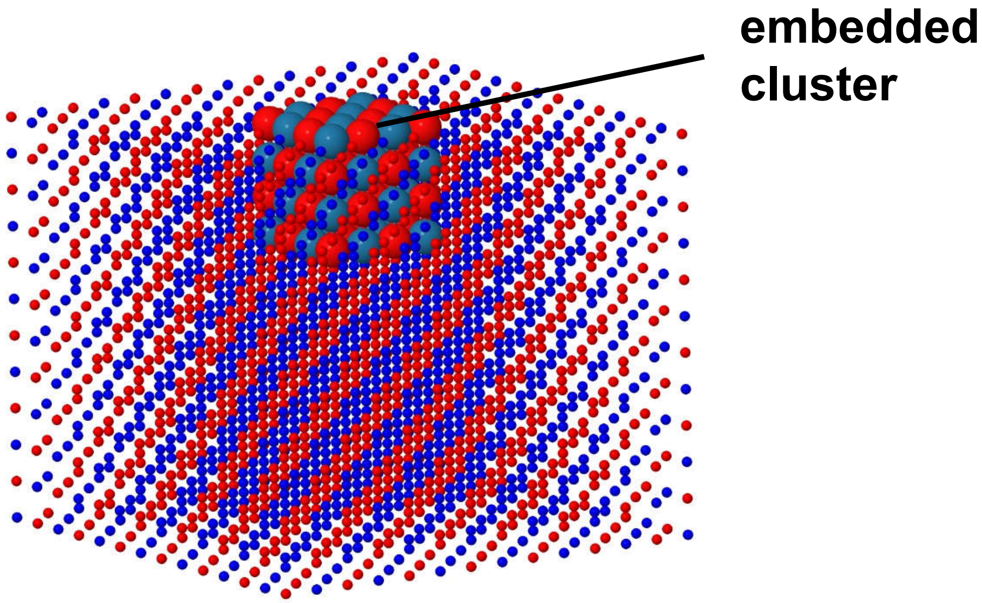
± defect-defect or adsorbate-adsorbate interaction

2) Cluster model:

+ isolated defects or adsorbates

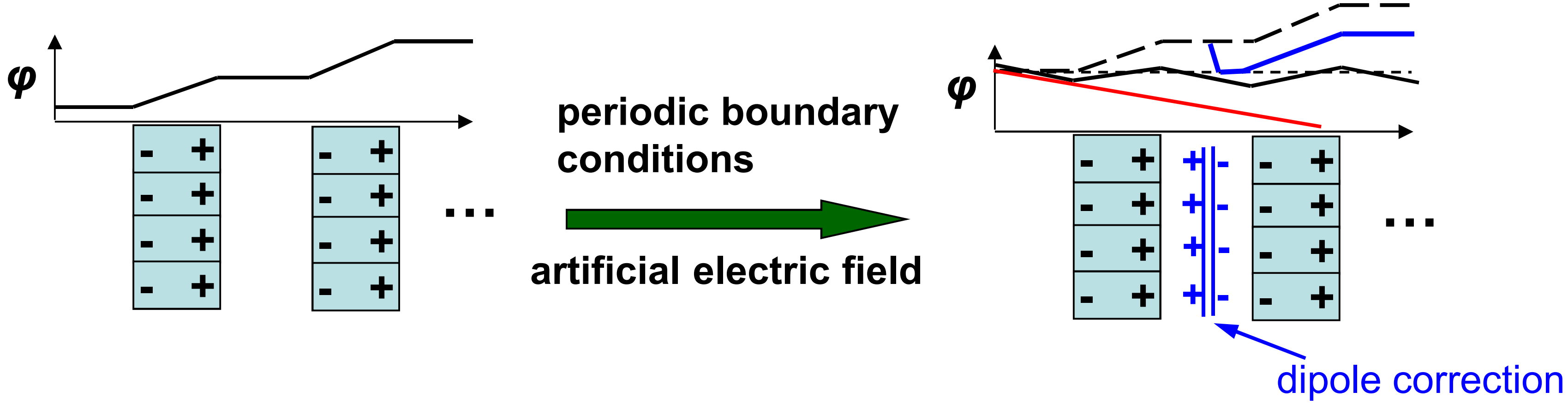
- border effects

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)

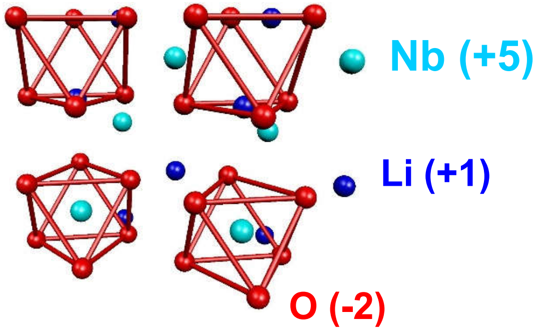


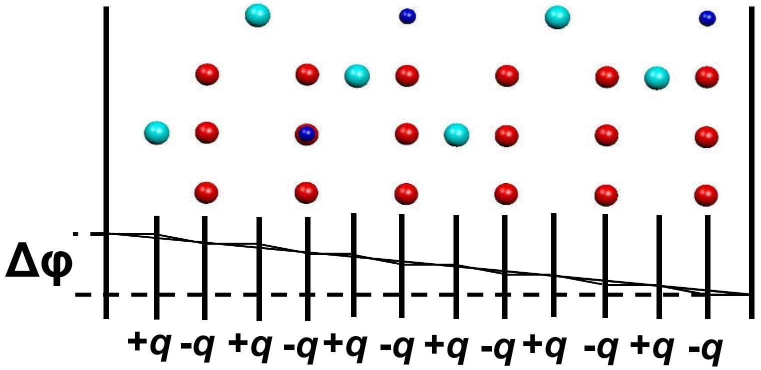
periodic boundary conditions

artificial electric field

dipole correction

4) Surface polarity

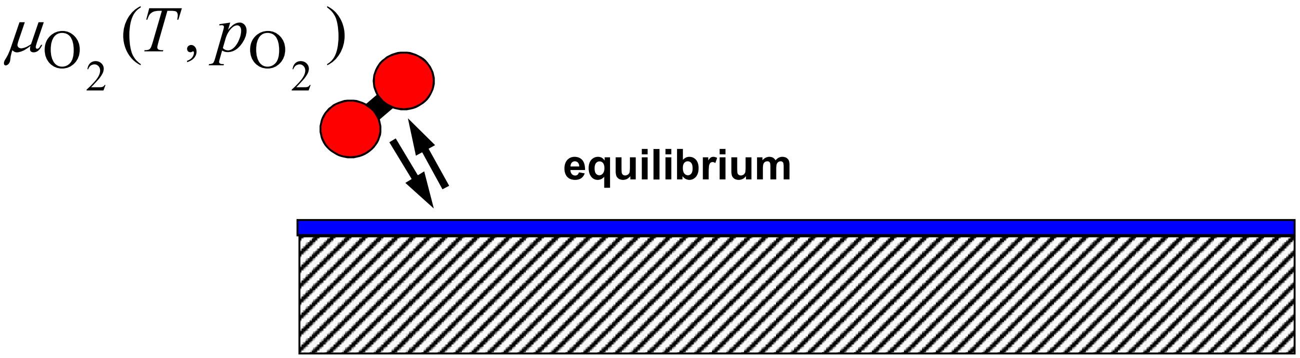




Thermodynamics

❐ 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

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

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

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

$\mu_O(T,p)$ - ?

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

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

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

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

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

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

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 (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 $\mu_{vib} = \frac{\hbar\omega}{2} + kT\ln\left(1 - e^{-\hbar\omega/kT}\right)$

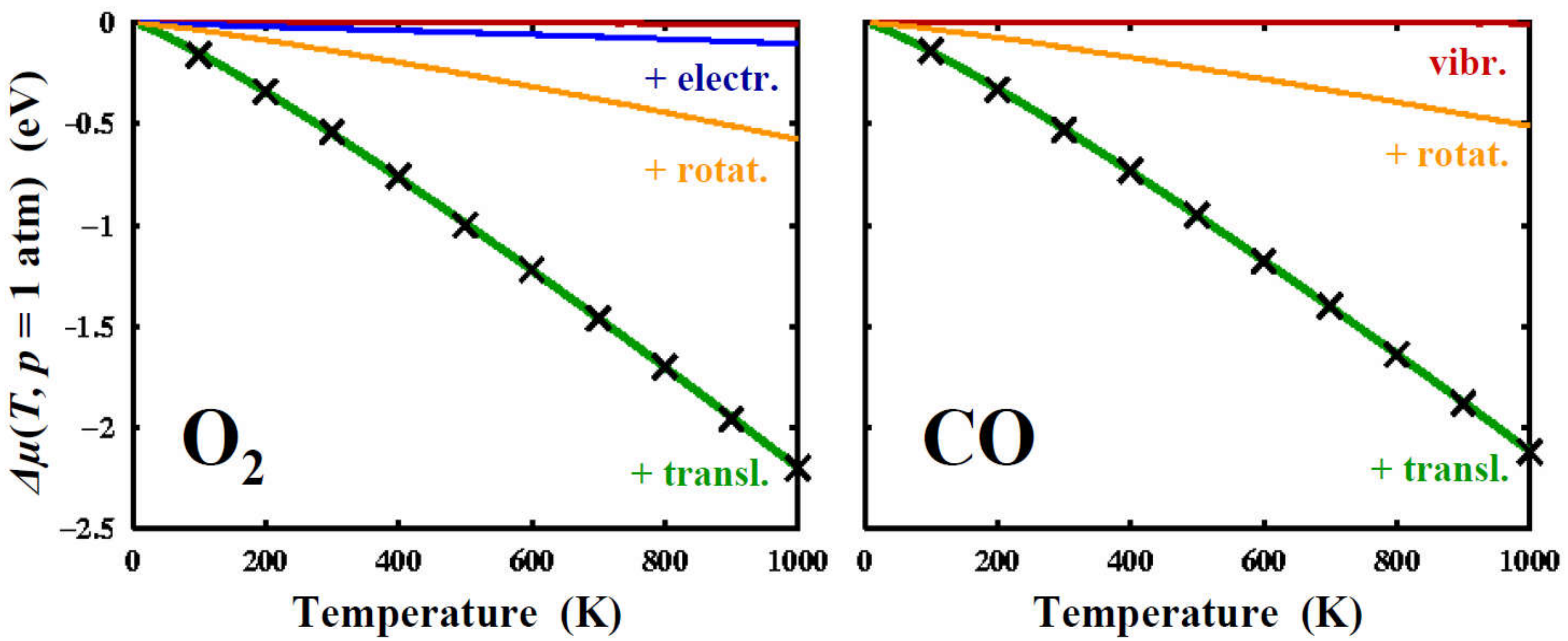
required input - vibrational frequency ω

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



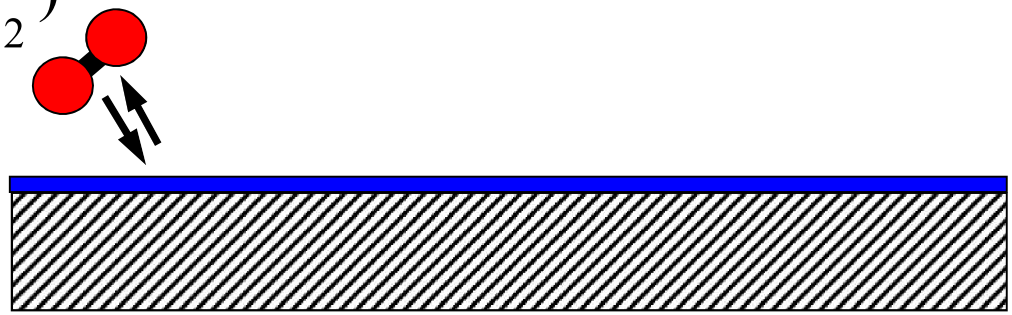
Alternatively: $\Delta\mu(T,p) = \Delta\mu(T,p^{O}) + k_{B}T\ln(p/p^{O})$

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

Thermodynamics

- ***Ab initio* atomistic thermodynamics**

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



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

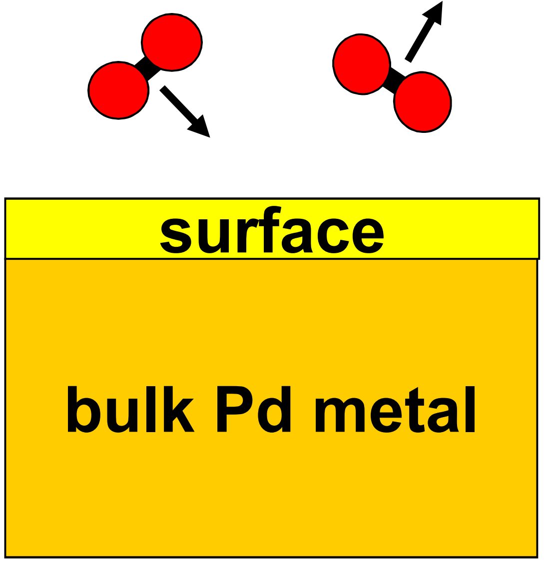
electronic structure calculations

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



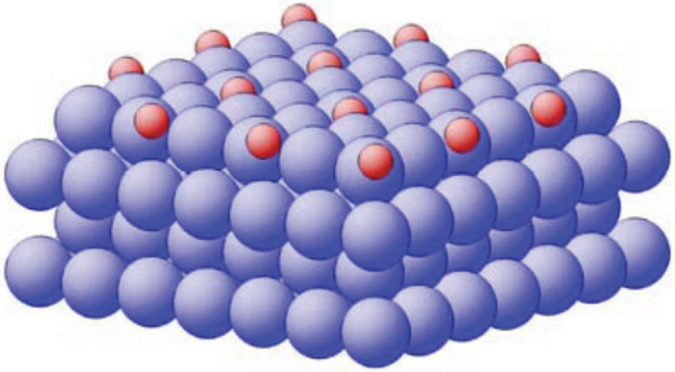
Reservoir: $\mu_O(T, p_{O_2})$ from ideal gas, $N_O^{ref} = 0$ (bare metal surface is the reference system), $\frac{1}{2}E_{O_2}$ is the reference for the chemical potential of O: $\mu_O = \Delta\mu_O + \frac{1}{2}E_{O_2}$

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

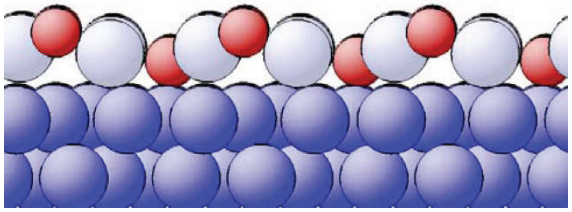
$$\Delta\gamma(T, p_{O_2}) = \frac{1}{A}\left[E_{surf}(N_O) - E_{surf}(0) - N_O \frac{1}{2} E_{O_2}\right] - \frac{1}{A} N_O \Delta\mu_O(T, p_{O_2})$$

Example: Pd(100)

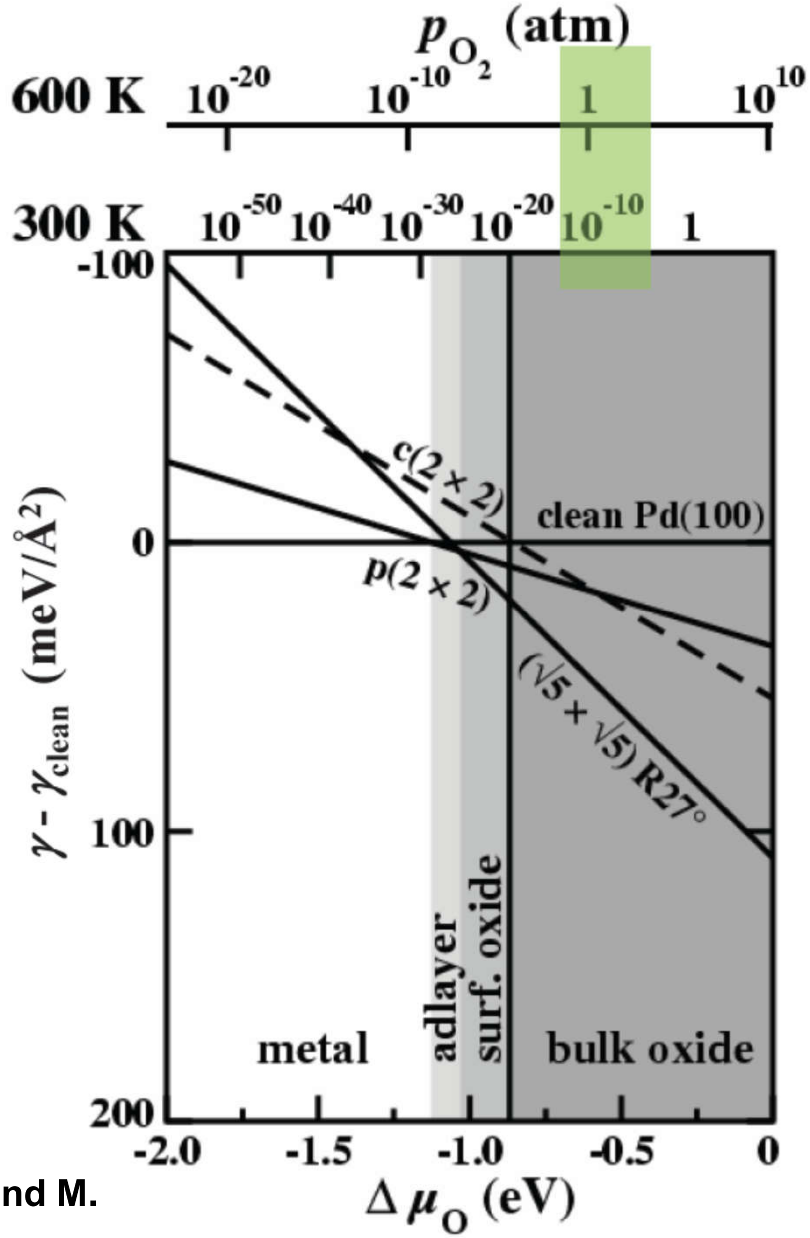
$$\Delta\gamma(T,p_{O_2}) = \frac{1}{A}\Delta E_{surf}(N_O) - \frac{1}{A}N_O\Delta\mu_O(T,p_{O_2})$$



p(2x2) O/Pd(100)



(√5x√5)*R*27° PdO(101)/Pd(100)

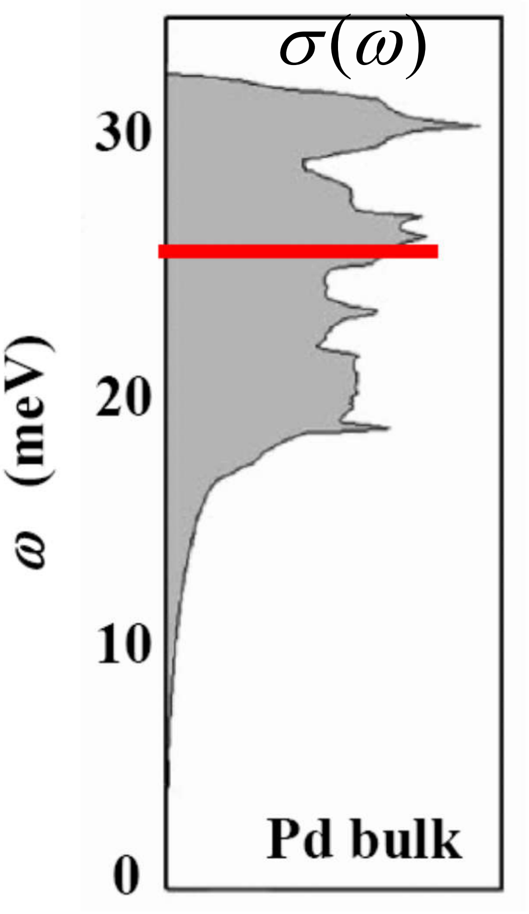


M. Todorova *et al.*, Surf. Sci. 541, 101 (2003); K. Reuter and M. Scheffler, Appl. Phys. A 78, 793 (2004)

Thermodynamics

- ***Ab initio* atomistic thermodynamics**

Vibrational contributions to the surface free energy:



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

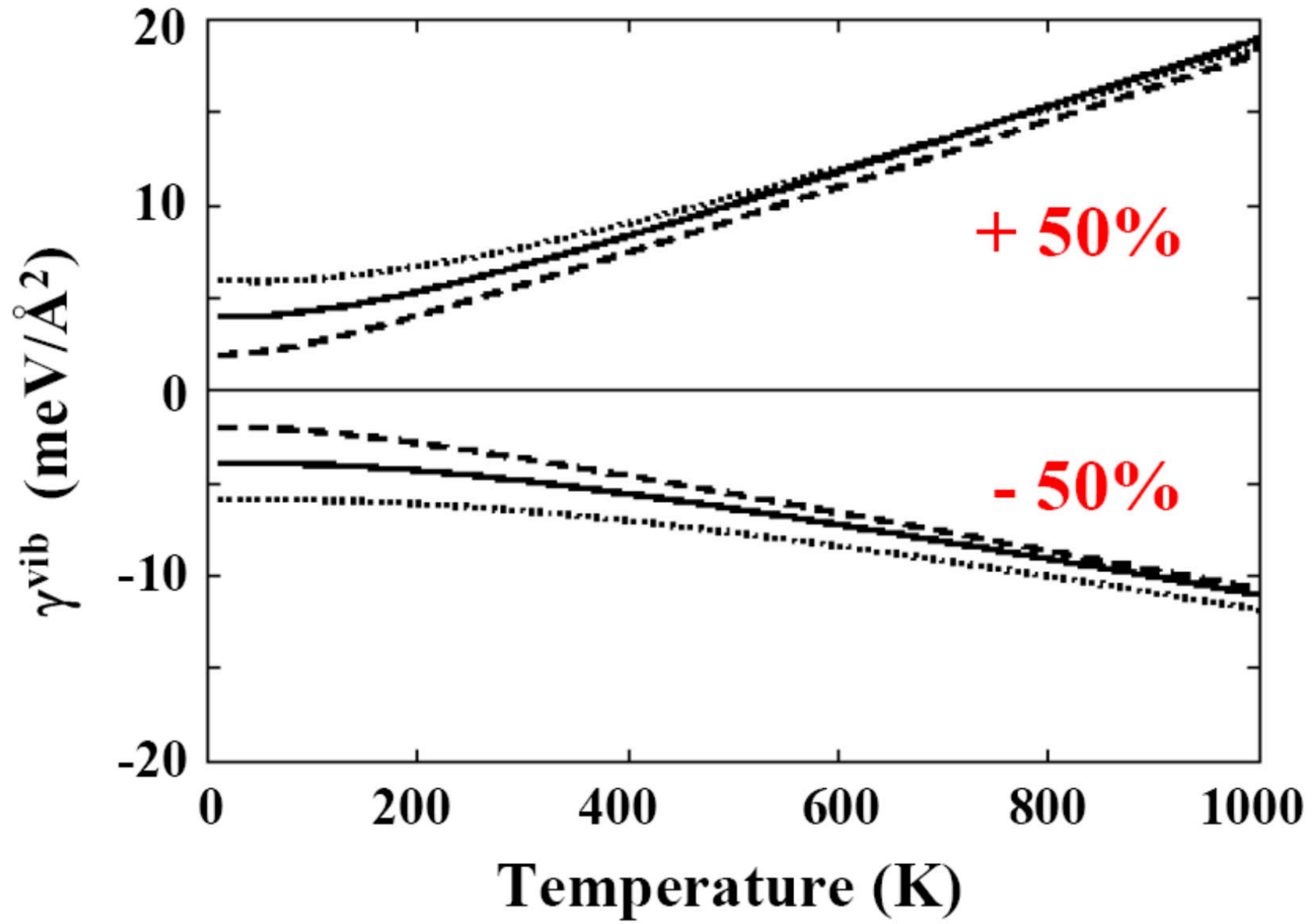
Only *changes* in vibrational free energy contribute to the surface free energy

Make estimate from simple models

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

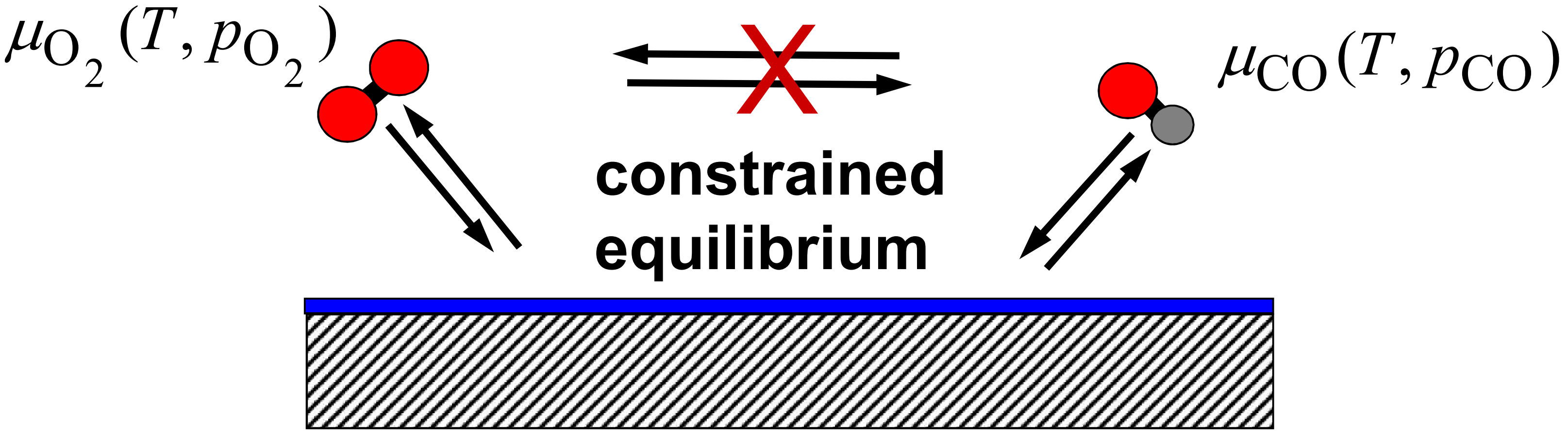
$\langle\omega\rangle_{\mathrm{Pd}}$**(bulk) ~ 25 meV**

Surface-induced variations of substrate modes



< 10 meV/Å^2 for T = 600 K – in this case!!!

First-principles atomistic thermodynamics: constrained equilibria



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

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

constrained equilibrium

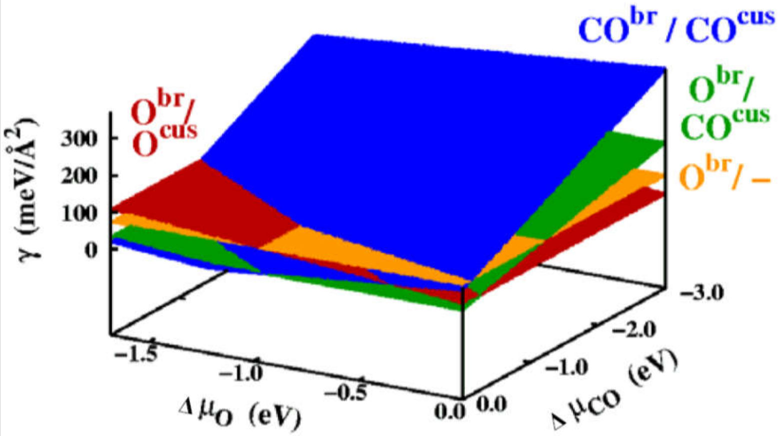
$$\Delta\gamma(T, p_{O_2}) = \frac{1}{A}\left[E_{surf}(N_O, N_{CO}) - E_{surf}^{ref} - N_O \frac{1}{2} E_{O_2} - N_{CO} E_{CO}\right]$$

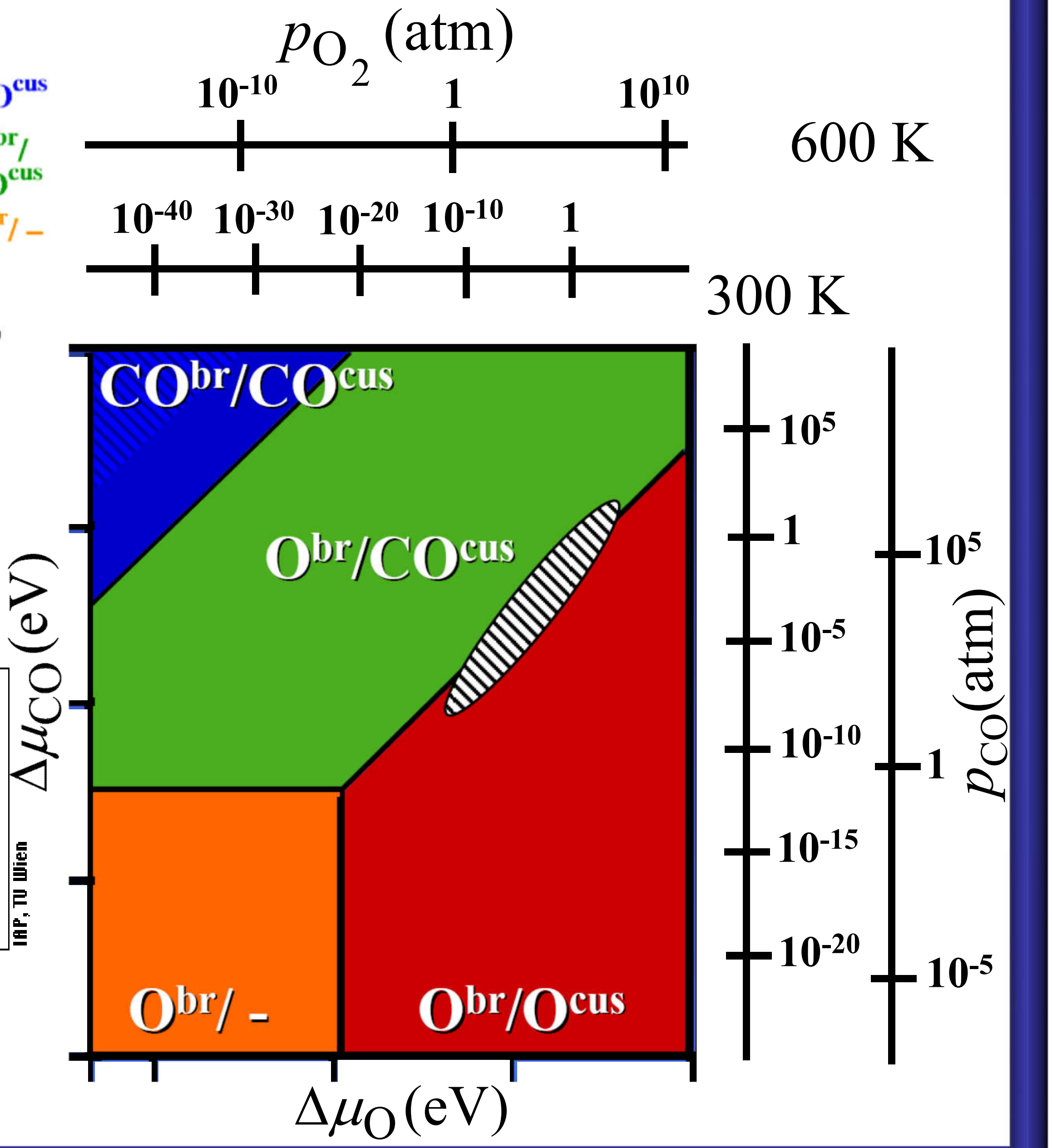
$$-\frac{1}{A} N_O \Delta\mu_O(T, p_{O_2}) - \frac{1}{A} N_{CO} \Delta\mu_{CO}(T, p_{CO})$$

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

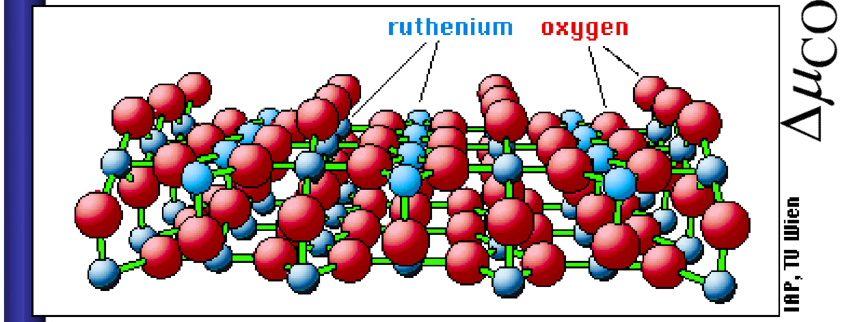
K. Reuter and M. Scheffler, Phys. Rev. B 65, 035406 (2001); Phys. Rev. B 68. 045407 (2003)

Surface phase diagrams



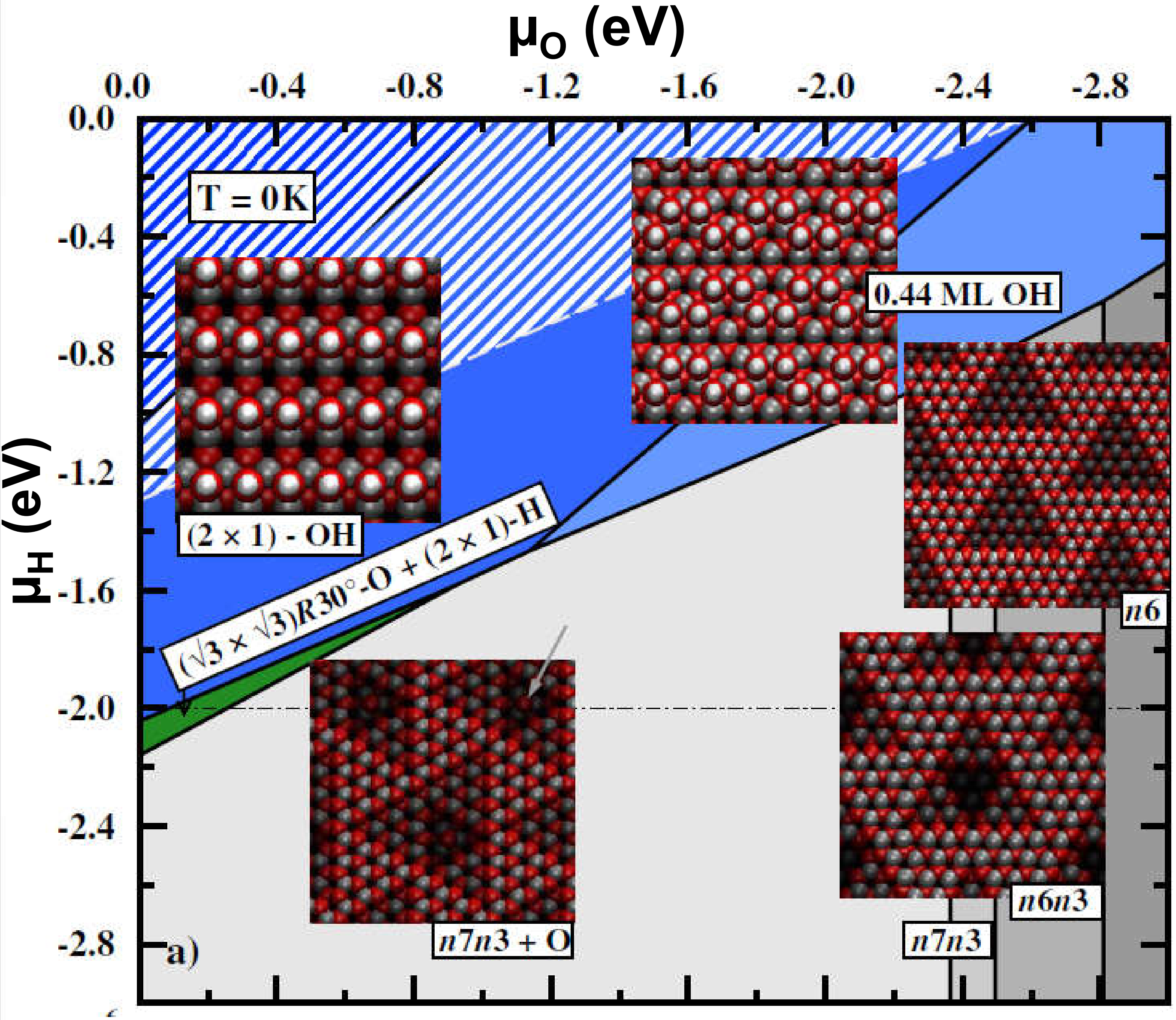


CO oxidation on $RuO_2(110)$



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

When vibrations do matter

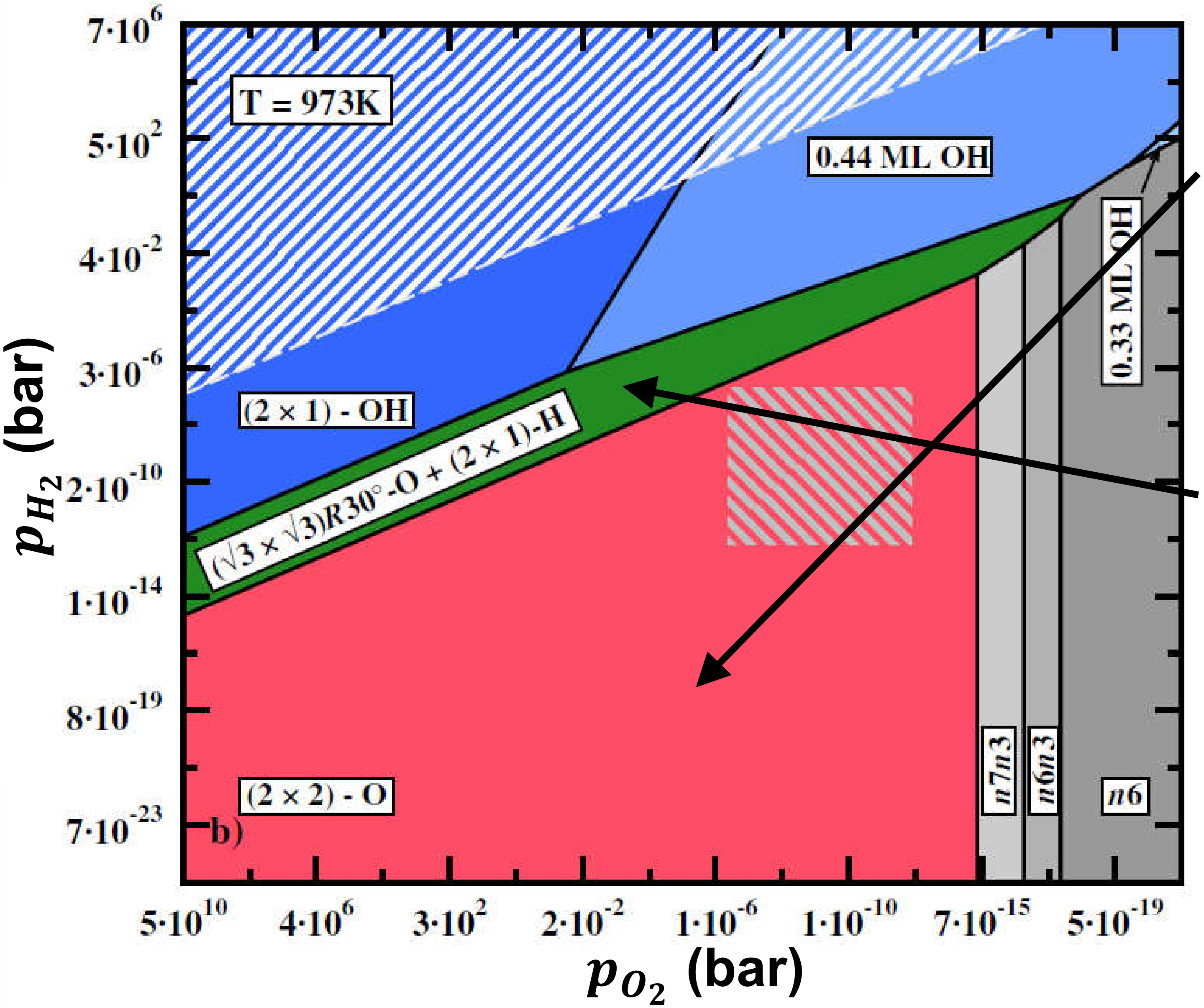


ZnO (0001) surface phase diagram in H_2O-O_2 atmosphere – no vibrations

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

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

When vibrations do matter



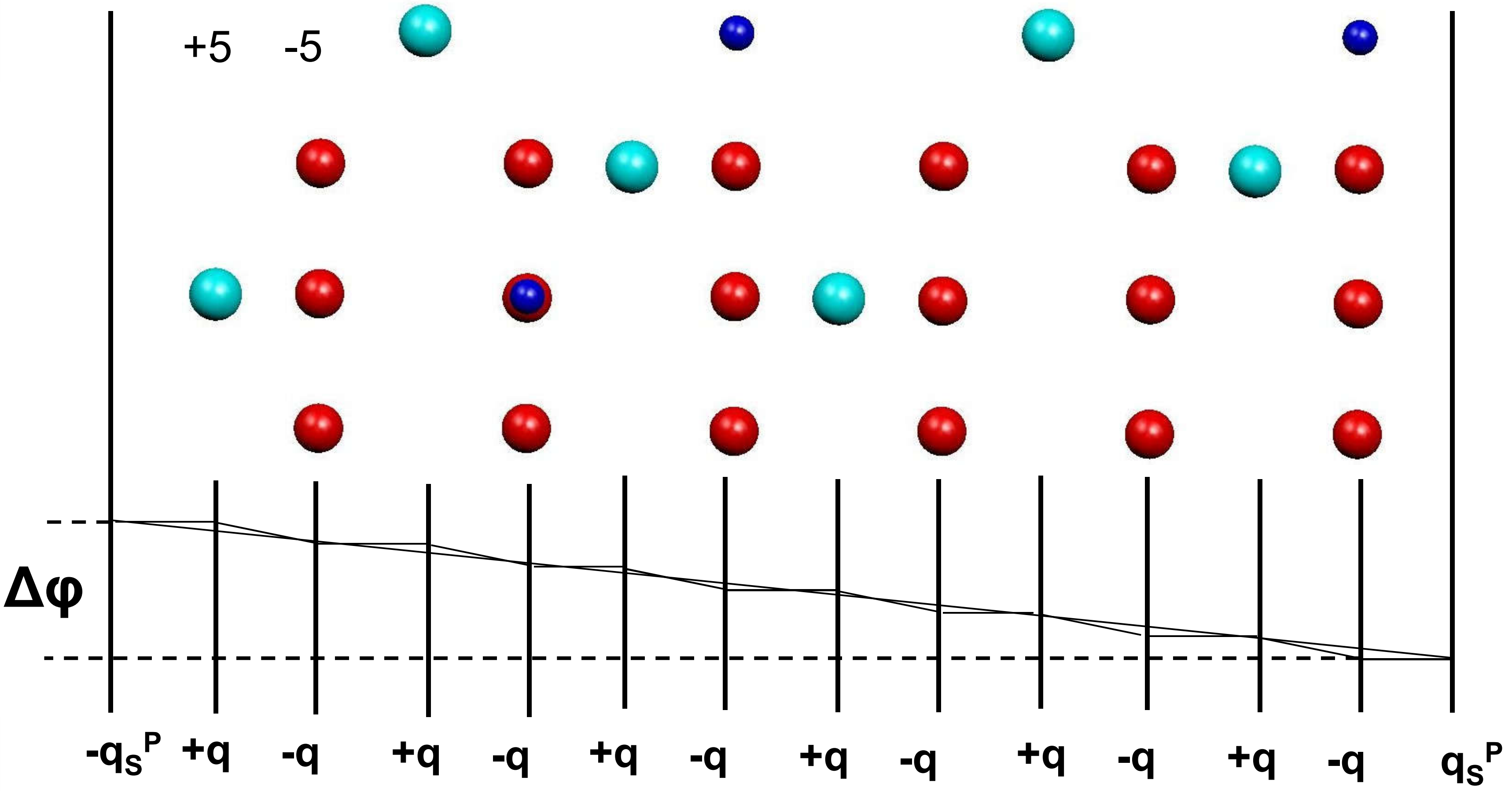
A (2x2)-O adlayer structure is stabilized by vibrational entropy effects

Observed at “humid” conditions

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

Polar surfaces

Paraelectric lithium niobate ($LiNbO_3$) stoichiometric surfaces:

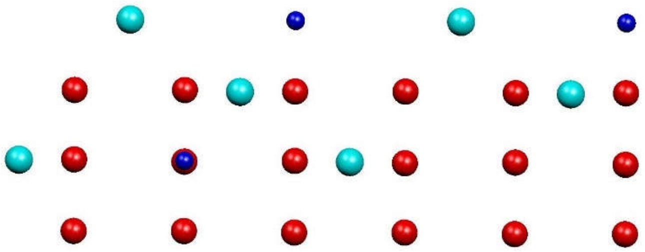


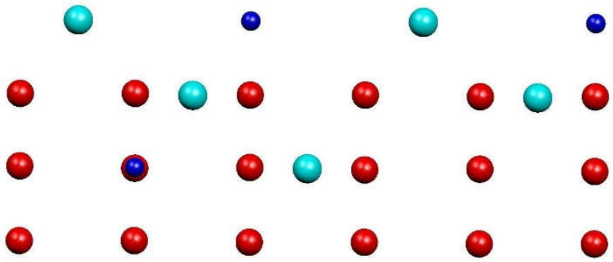
$q_S^P = -q/2 \approx -2.5e \neq 0$ – surface charge, $P_{PE} \neq 0$

$\Delta\varphi \approx 250$ V >> $E_g/e \approx 3.7$ V → surface charge almost completely passivated

Polar surfaces

Where to cut?





Charge = 0,

Dipole moment ≠ 0

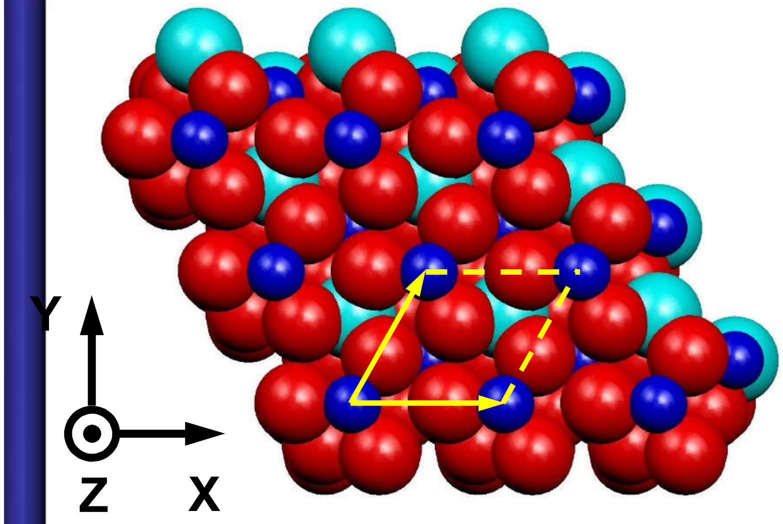
Charge = -5e,

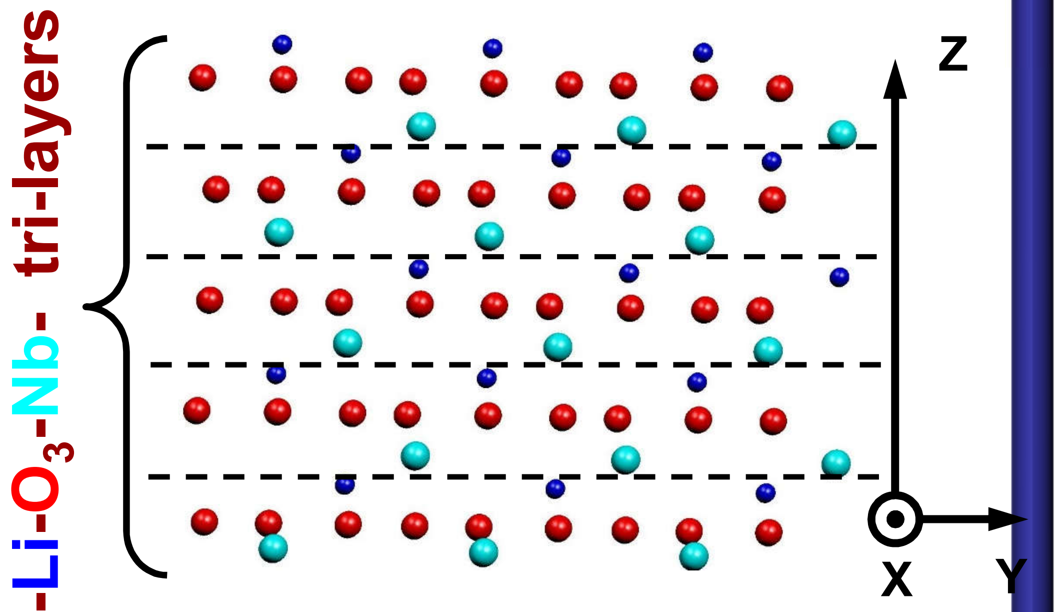
Dipole moment = 0

Surface charge = ± 2.5e

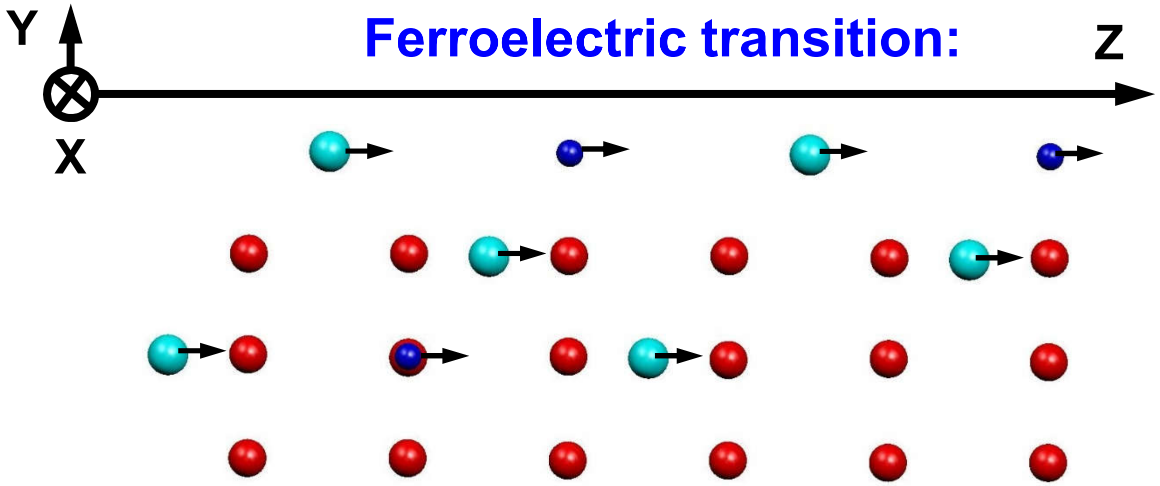
Ferroelectric lithium niobate $LiNbO_3$.

Unrelaxed stoichiometric surface and layer stacking:



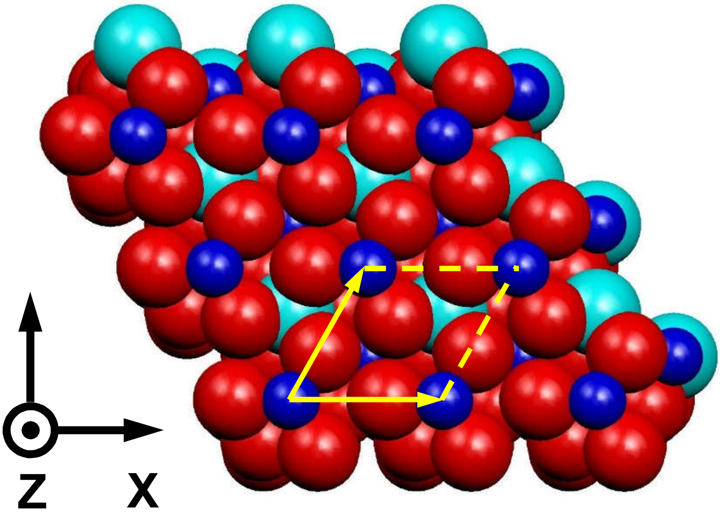


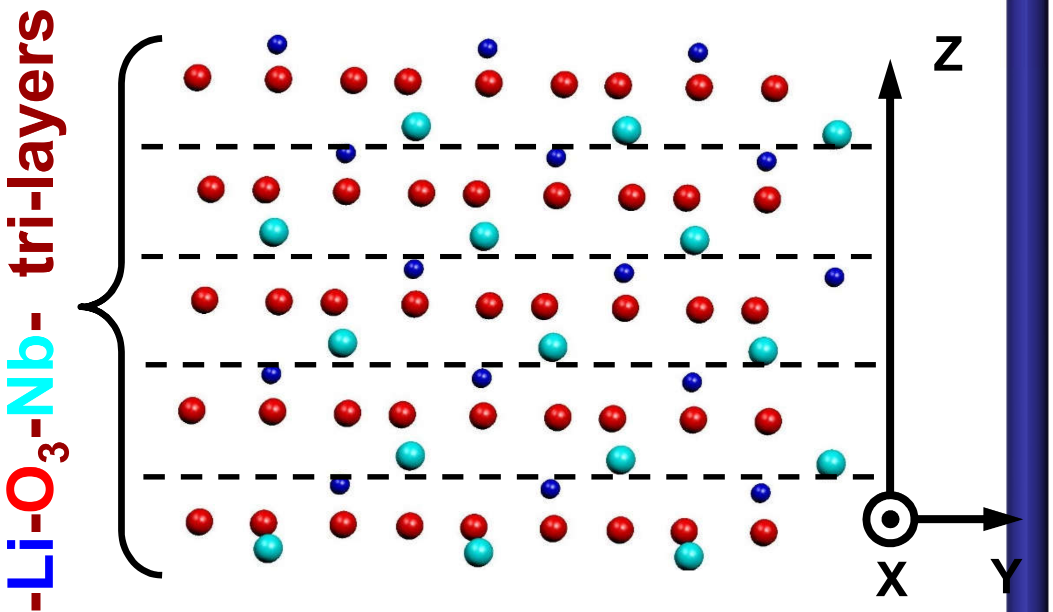
Ferroelectric transition:



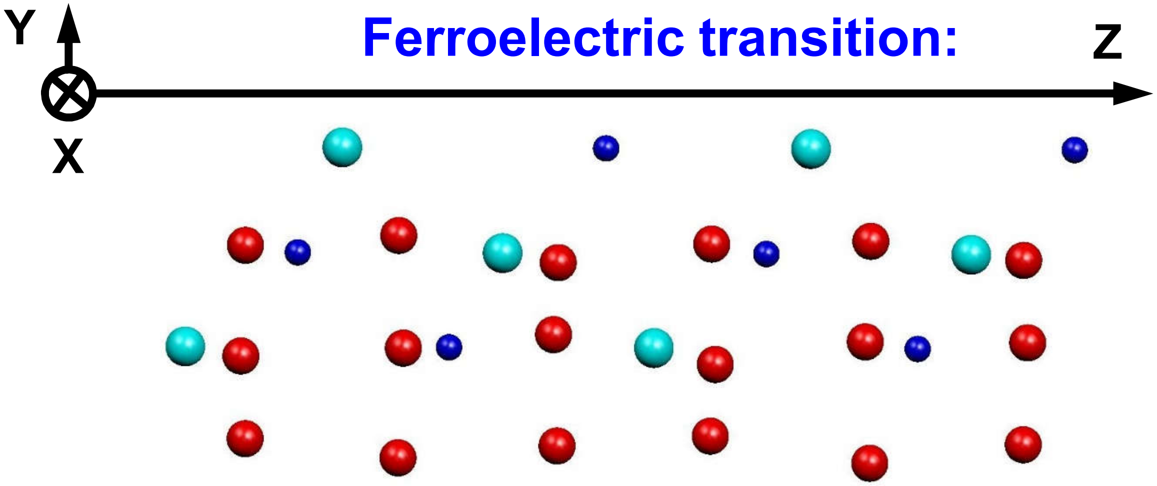
Ferroelectric lithium niobate $LiNbO_3$

Unrelaxed stoichiometric surface and layer stacking:

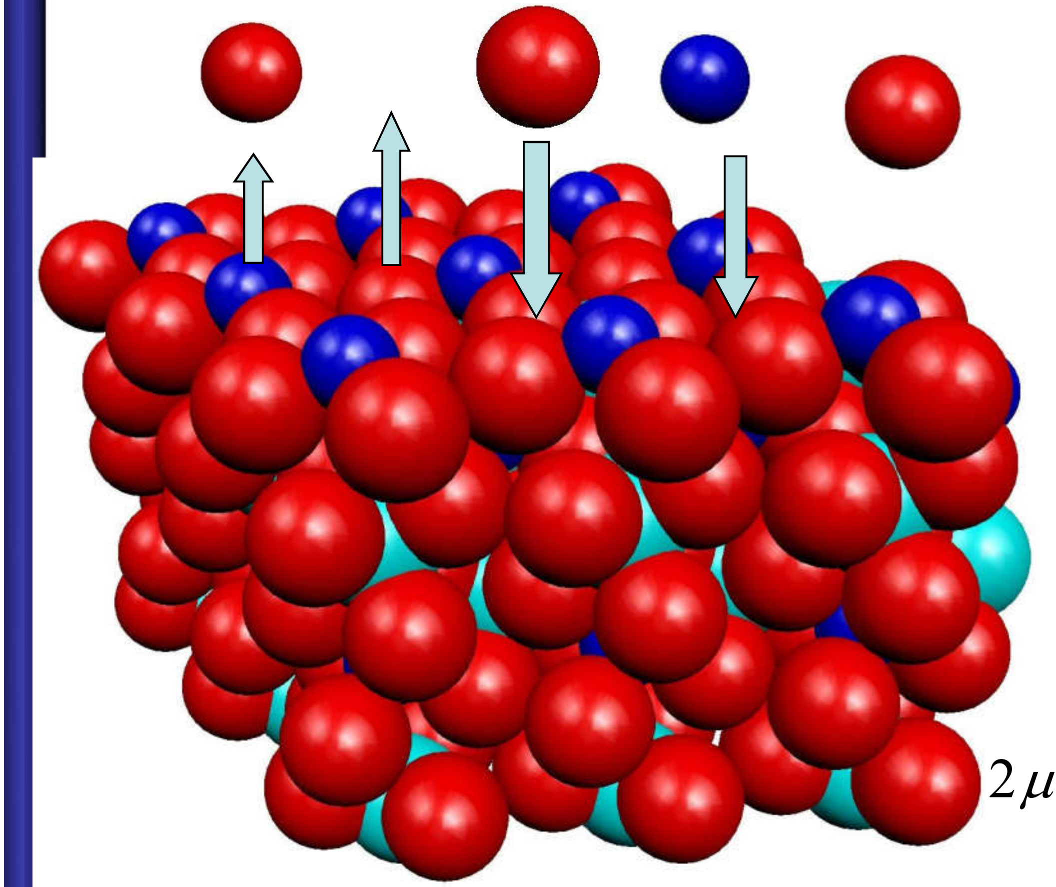




Ferroelectric transition:



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:

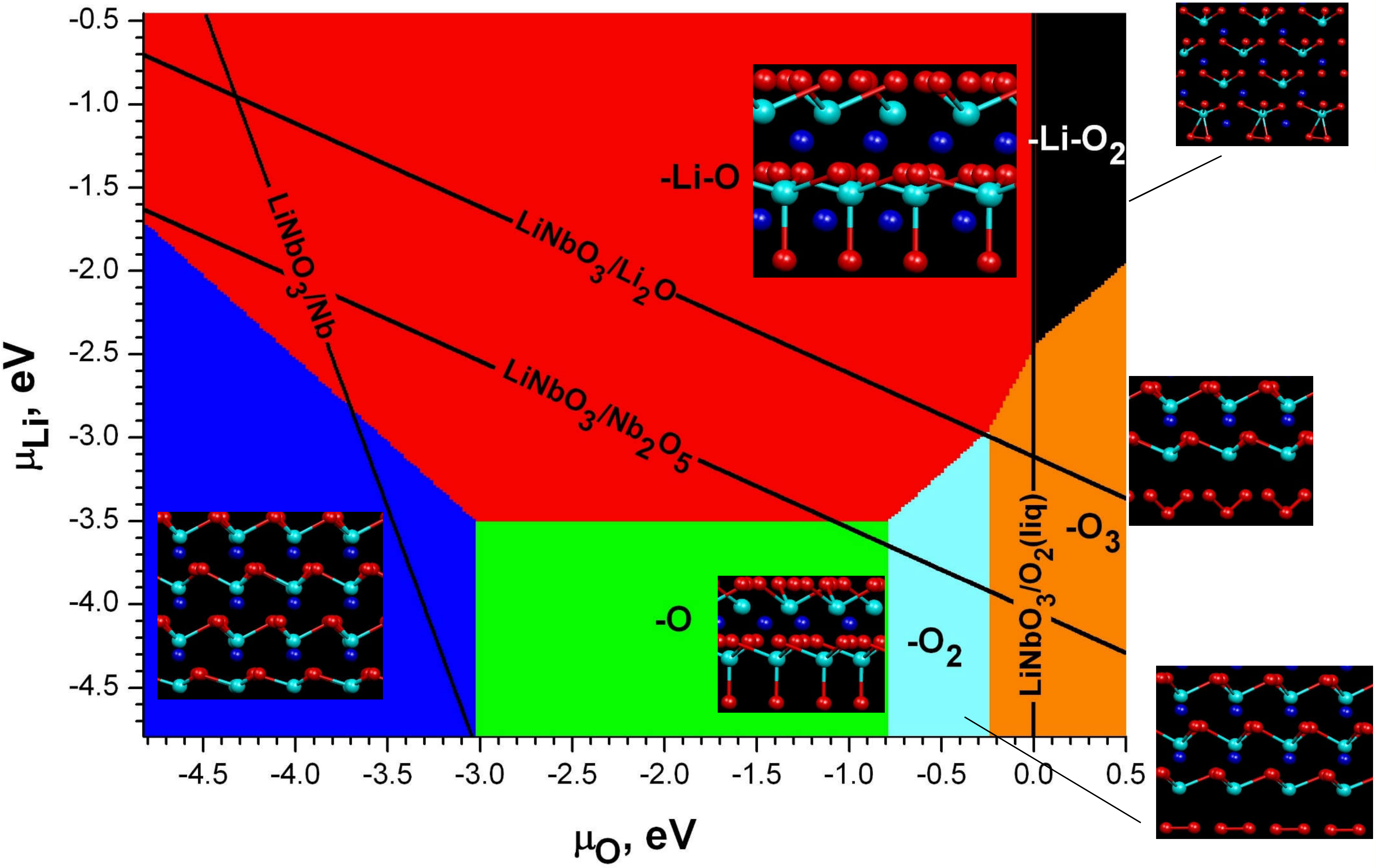
$$2\mu_{Li} + \mu_O < g_{Li_2O}^{bulk}, \quad 2\mu_{Nb} + 5\mu_O < g_{Nb_2O_5}^{bulk}$$

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

Surface free energy:

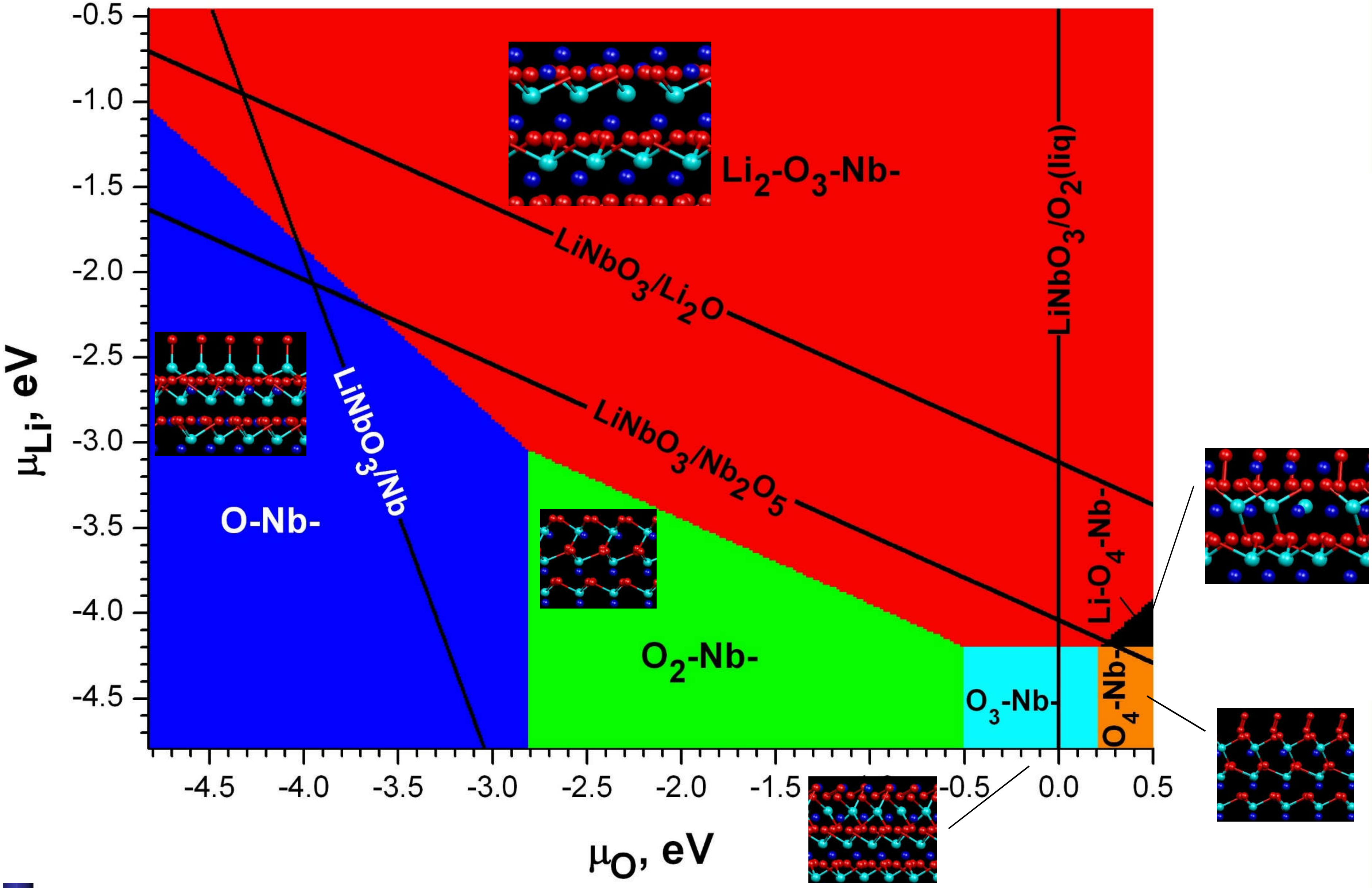
$$\gamma(T,p) = G^{slab}(N_{Nb}, N_{Li}, N_O) - \mu_{Nb}(T,p)N_{Nb} - \mu_{Li}(T,p)N_{Li} - \mu_O(T,p)N_O$$

Phase diagram for the *negative* surface



Levchenko, Rappe, PRL 100, 256101 (2008)

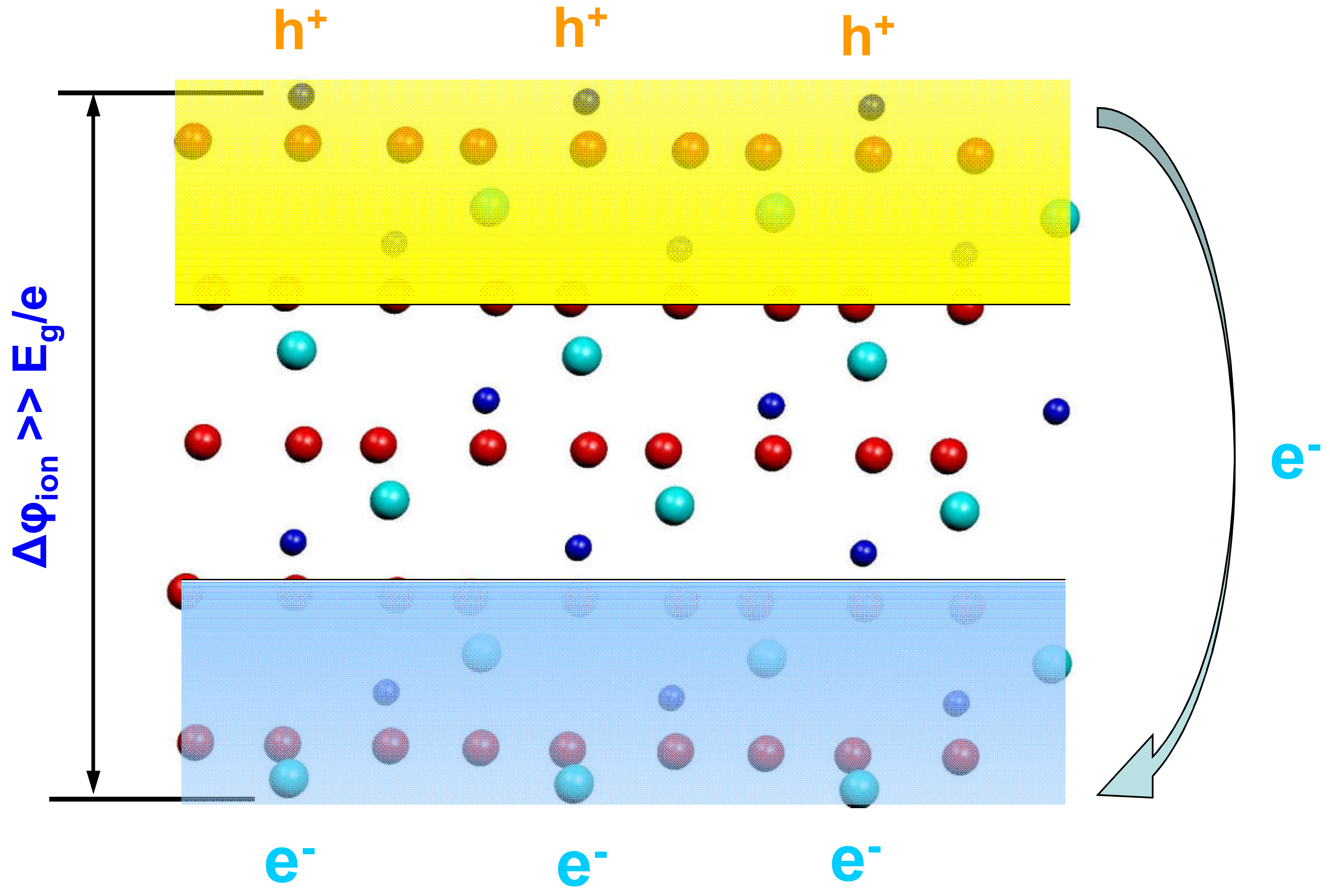
Phase diagram for the *positive* surface



Levchenko, Rappe, PRL 100, 256101 (2008)

Surface charge passivation

Fixed stoichiometry: surface charge passivated by electrons and holes.

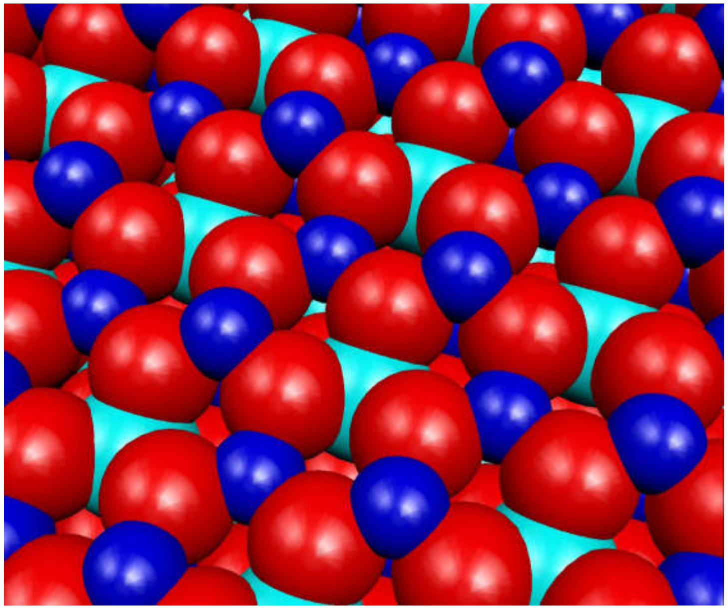


About 1e/unit cell is transferred

Most stable terminations: explanation

positive surface:

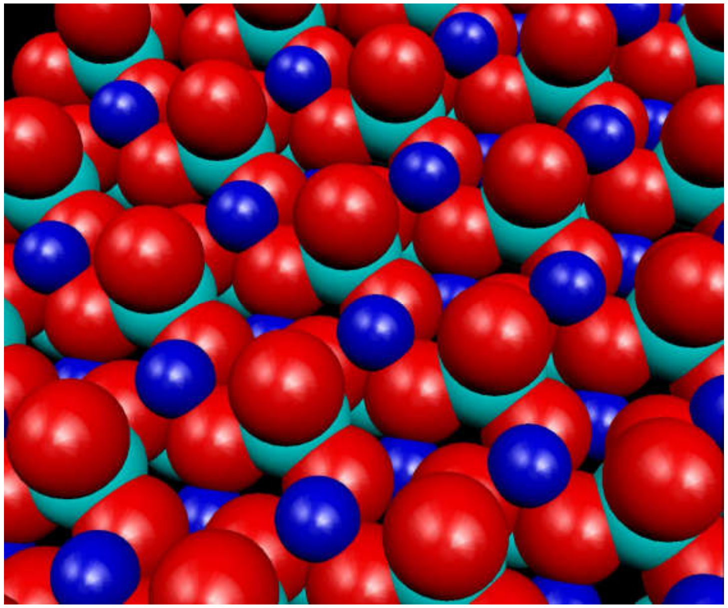
Li_2-O_3-Nb-



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

negative surface:

-Li-O



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)