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Ab initio calculations at interfaces

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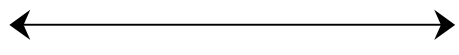
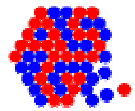
Theme

Atomistic Calculations  Gibbs' thermodynamics



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See website for publications

Thanks!

ASG staff:

Ali Alavi (now Cambridge)

Sasha Lozovoi

Tony Paxton

Arnaud Marmier (now Bath)

Funding

EC: TMR, HCM } PSIK network

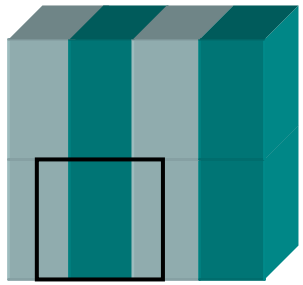
ESF:

EPSRC

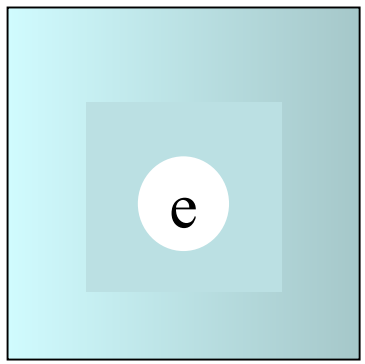
Ab initio

Periodic boundary conditions

~10-500 atoms →

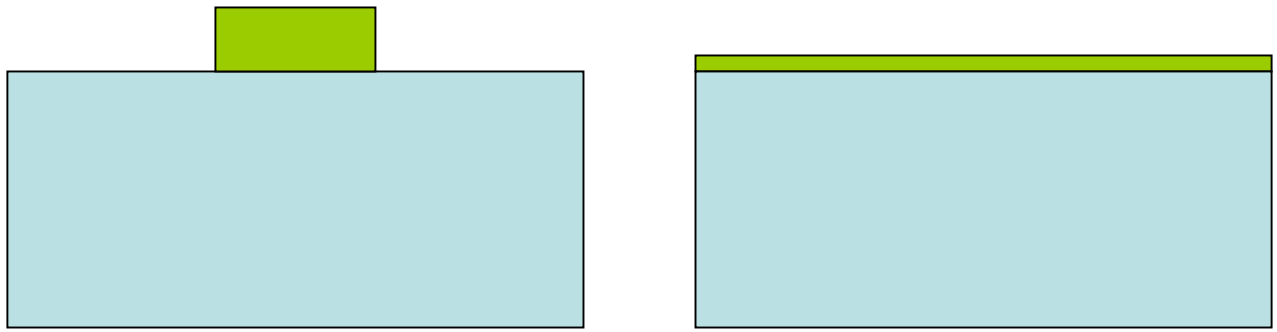


Local density approximation (LDA),
Generalised Gradient Approximation (GGA)



Codes: CASTEP, VASP, SIESTA, …

Growth mode:
Example of a field of application



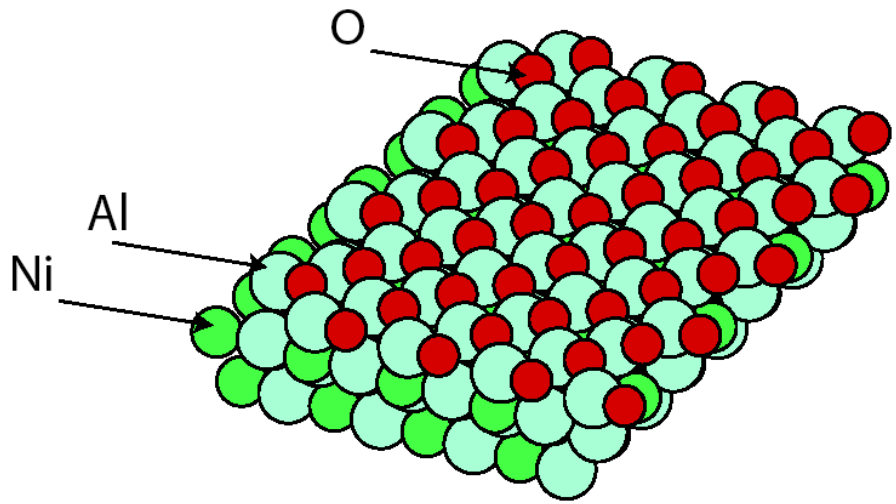
Island growth Layer-by-layer growth

How can we predict growth mode?

- Calculate **nanoscale** thermodynamic driving forces

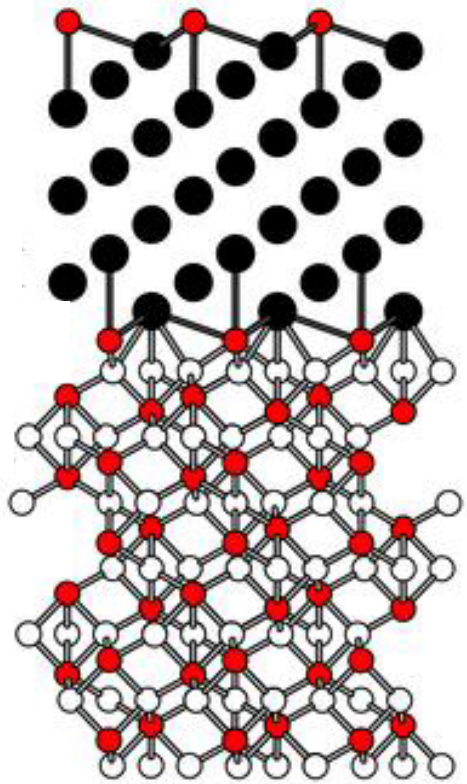
Applications and Methodology 1.

Oxide layer on NiAl(110)

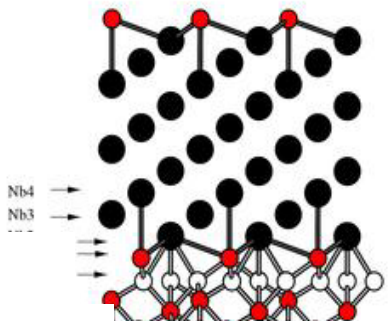


Applications and Methodology 2.

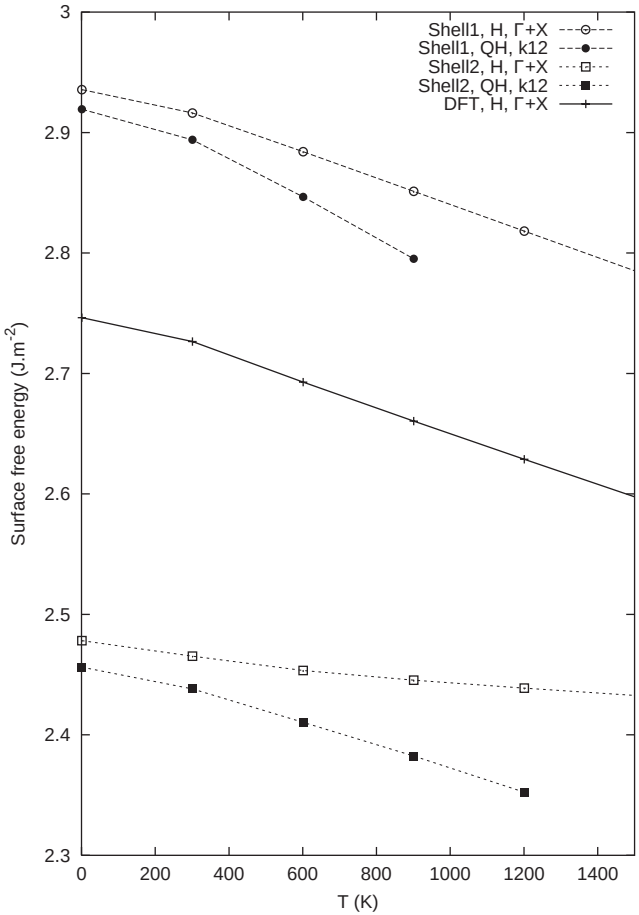
Nb(111)-Al2O3(0001) interface



Applications and Methodology 3.

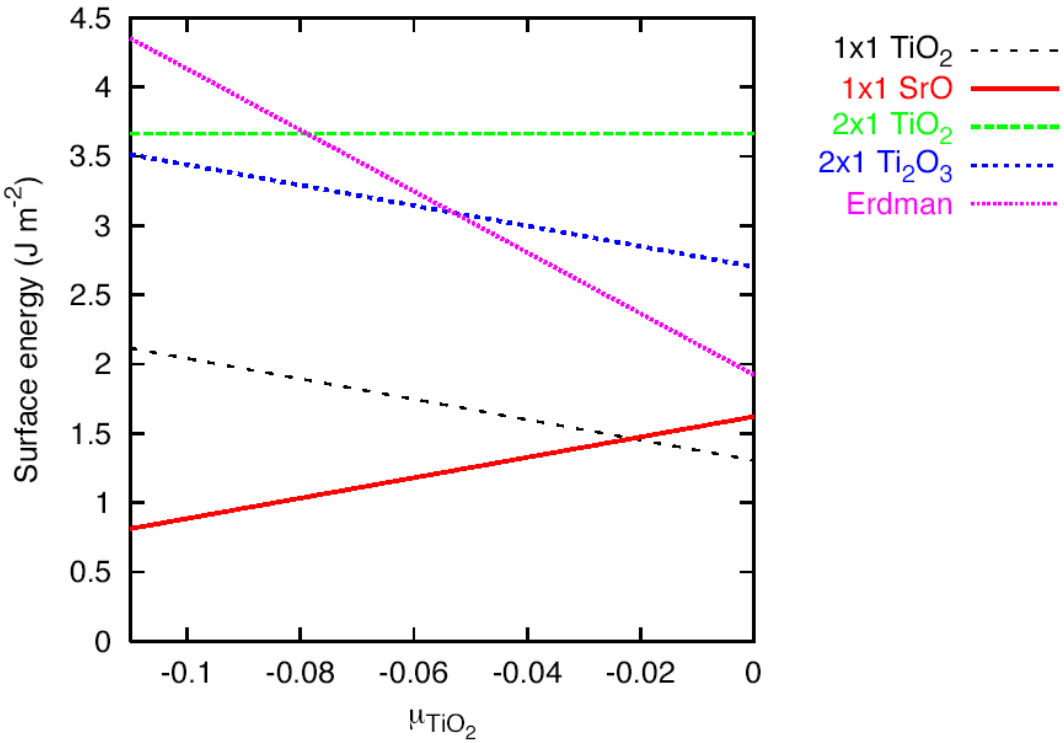


Alumina (0001) surface:
Energy versus temperature



Applications and Methodology 4.

Energy of SrTiO3 surfaces:
(work in progress)



Reference for interfaces:

Sutton, A. P. and R. W. Balluffi (1995).
Interfaces in Crystalline Materials. Oxford, Clarendon.

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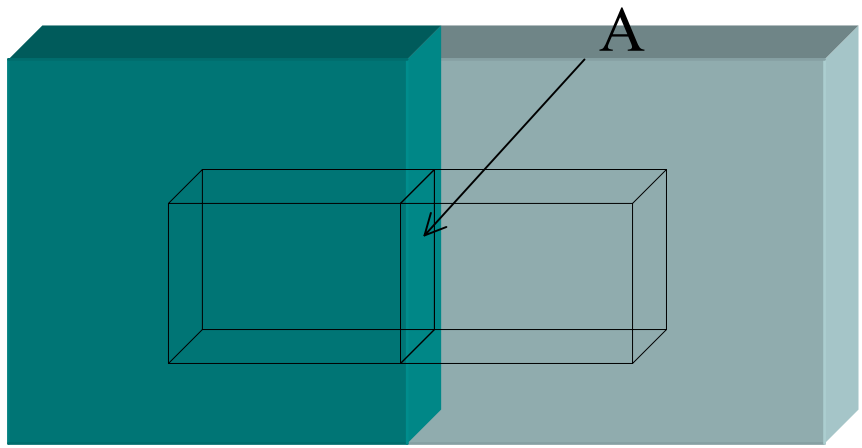
Definition of surface energy σ



For a planar interface, in general:

$$\sigma = (G_s - \sum_i N_i \mu_i) / A$$

Chemical potential of component *i*

Gibbs energy of whole box

Number of atoms of *i*

Calculate for different relaxed structures and stoichiometries.
Minimum σ is predicted equilibrium at given chemical potentials.

Contributions to surface free energy σ

Contributions we would like to know

- Internal energy
- ~~Configurational entropy of surface atoms~~ still too difficult!
- Configurational entropy of components in vapour
  (Example: partial pressure of oxygen)
- Configurational entropy of components in solid
  (Example: constitutional defects)
- Vibrational entropy (-TS)

Thermodynamic setup (NiAl)

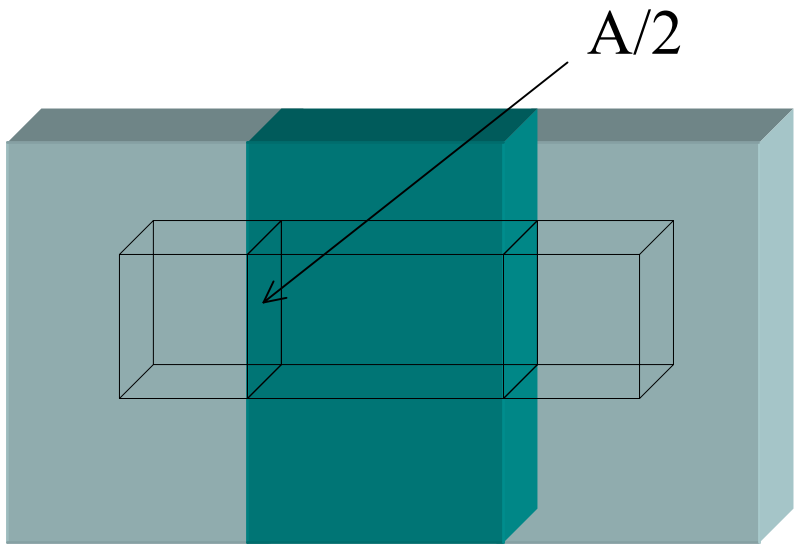
The oxidised surface (represented by a slab in calculations) is in equilibrium with bulk Ni_xAl_{1-x} and vapour with an oxygen partial pressure p_{O_2}

Phase Rule: Degrees of freedom = C-P+2 = 3.

We choose x, T and p_{O_2}

Definition of surface energy

Periodic Boundary Conditions

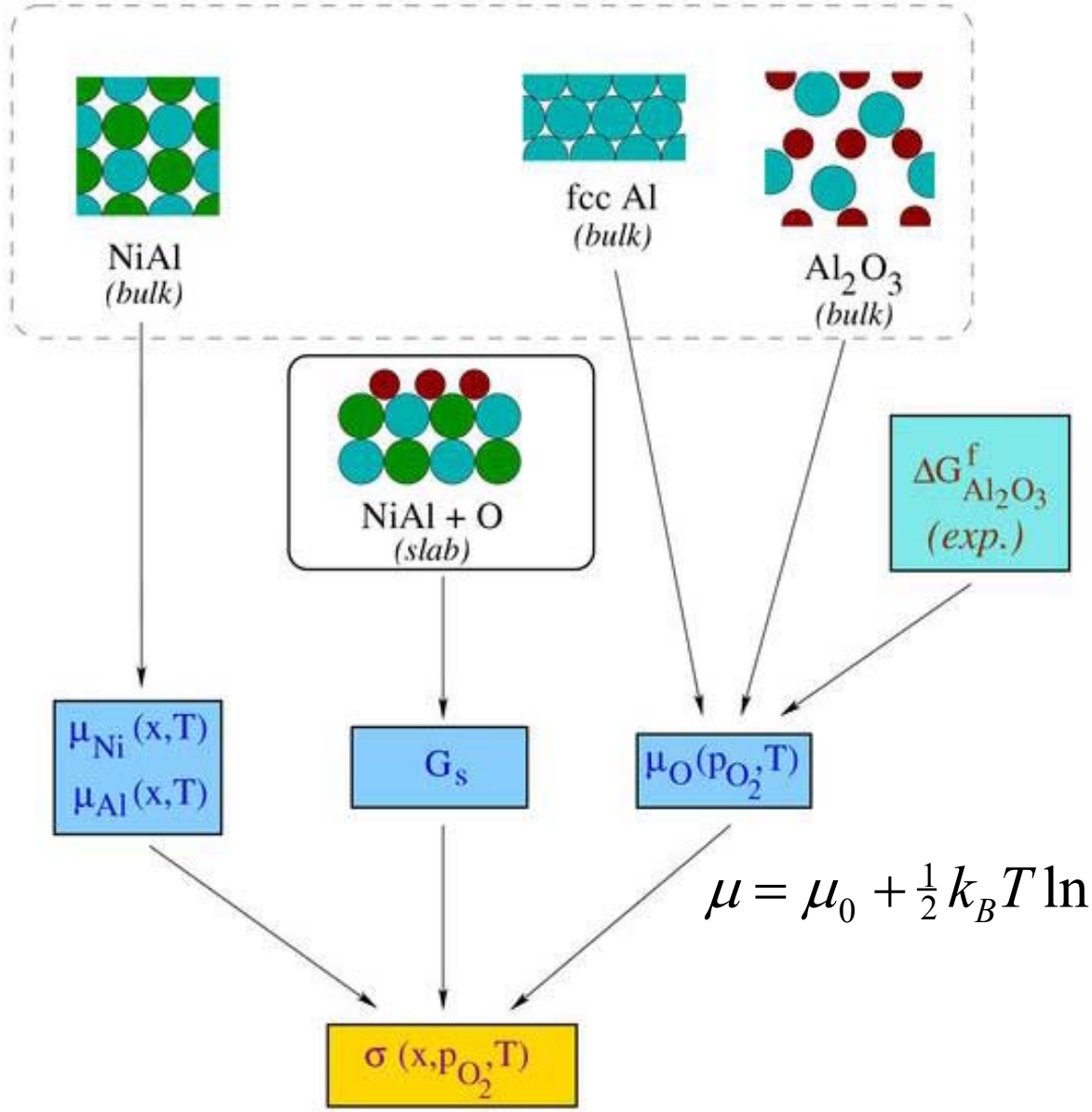


For NiAl:

$$\sigma(x,T,p_{O_2}) = (G_s - N_{Ni}\, g_{NiAl}) / A - \mu_{Al}(x,T)\Gamma_{Al} - \mu_O(p_{O_2},T)\Gamma_O$$

$$g_{NiAl} = \mu_{Ni} + \mu_{Al}$$

Scheme for σ calculation



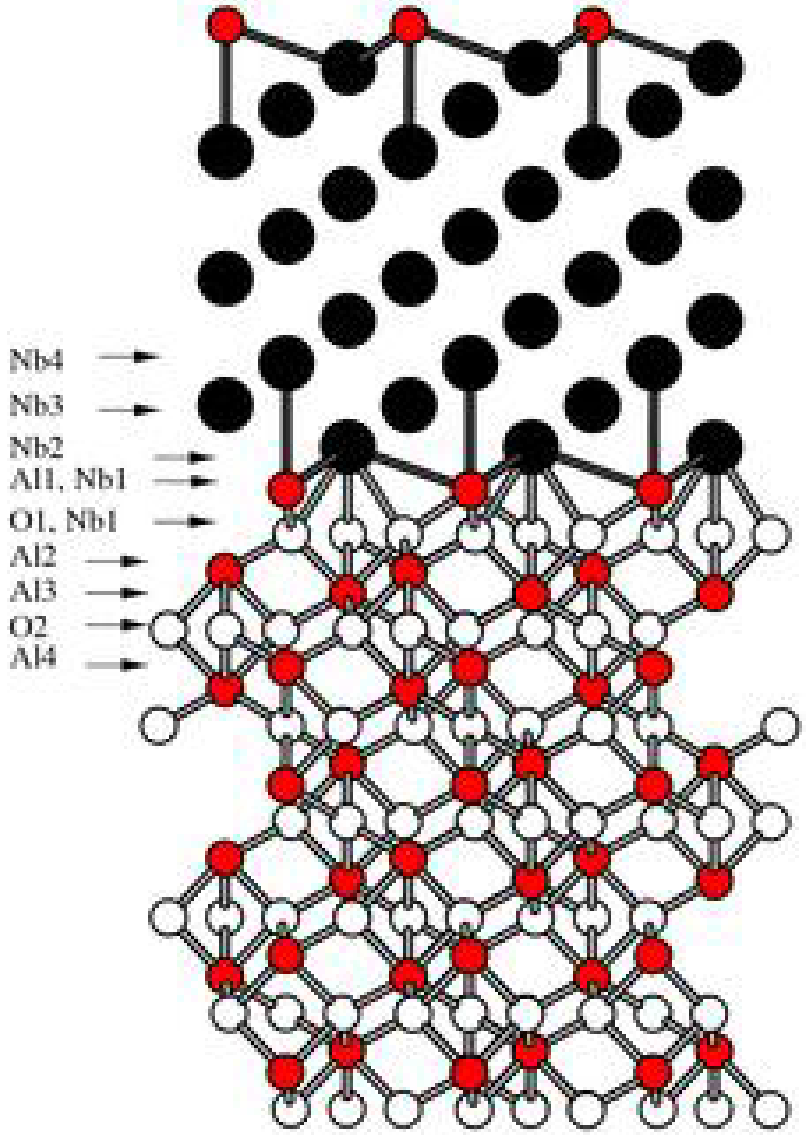
$$\mu = \mu_0 + \tfrac{1}{2} k_B T \ln\left(p_{O_2} / p_0\right)$$

Change in the point defect energies

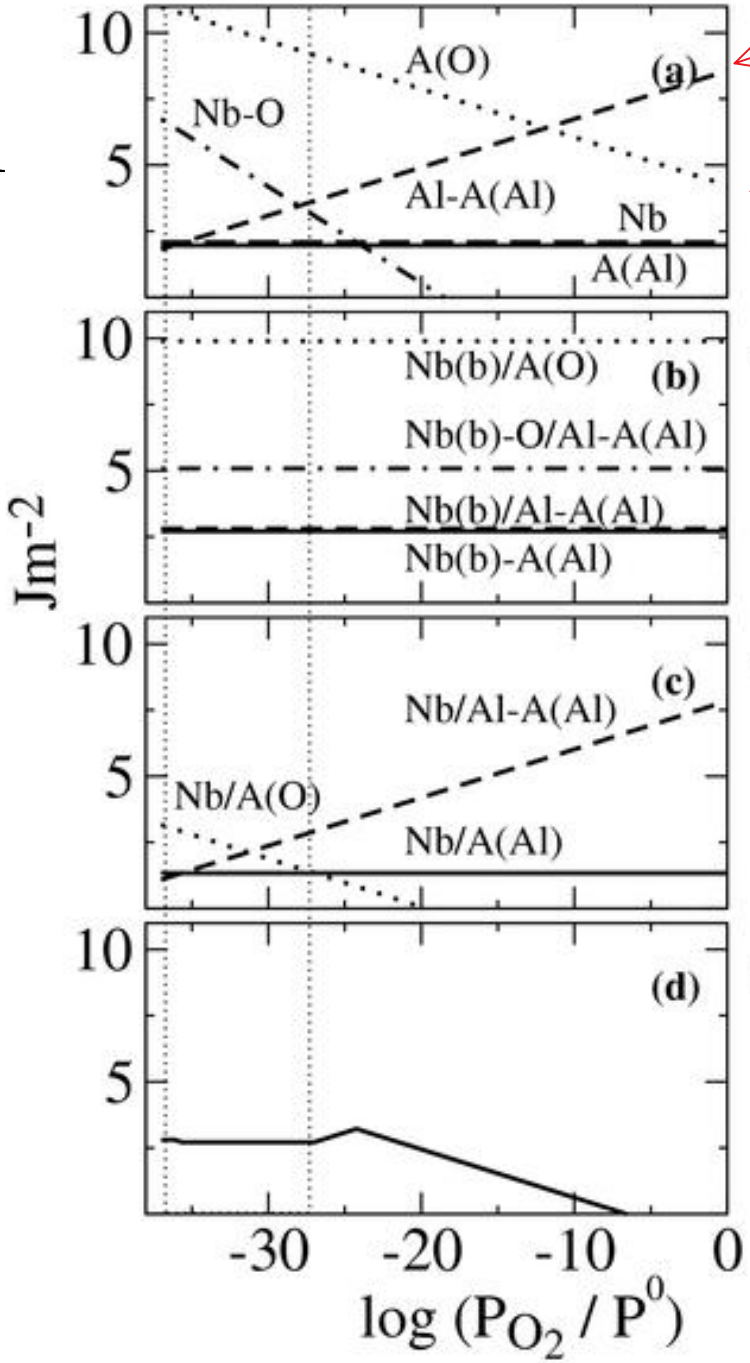
	ΔE, eV			
	bulk	free surface	1/3 ML of O	1 ML of O
Exchange defect: $Ni_{Al}^{(2)} + Al_{Ni}^{(1)}$	+ 2.66	+1.26	+ 0.42	**– 1.87 (!)**
V_{Ni} at the surface:				
bulk → 1st layer	—	– 0.13	– 0.52	**– 2.96 (!)**
bulk → 2nd layer	—	+ 0.04		– 0.51

Thus, there is a strong desire of the oxidizing NiAl surface to get rid of Ni in the top layer.

Nb(111)-Al2O3(0001) interface



Interfacial energies



Al-rich

Surface free energies

O-rich

Stoichiometric

Works of Separation

Works of Adhesion

Interface free energy

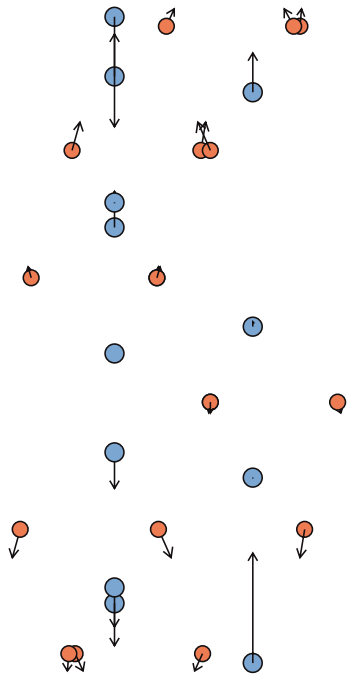
Vibrational contribution to σ

Quasiharmonic approximation:

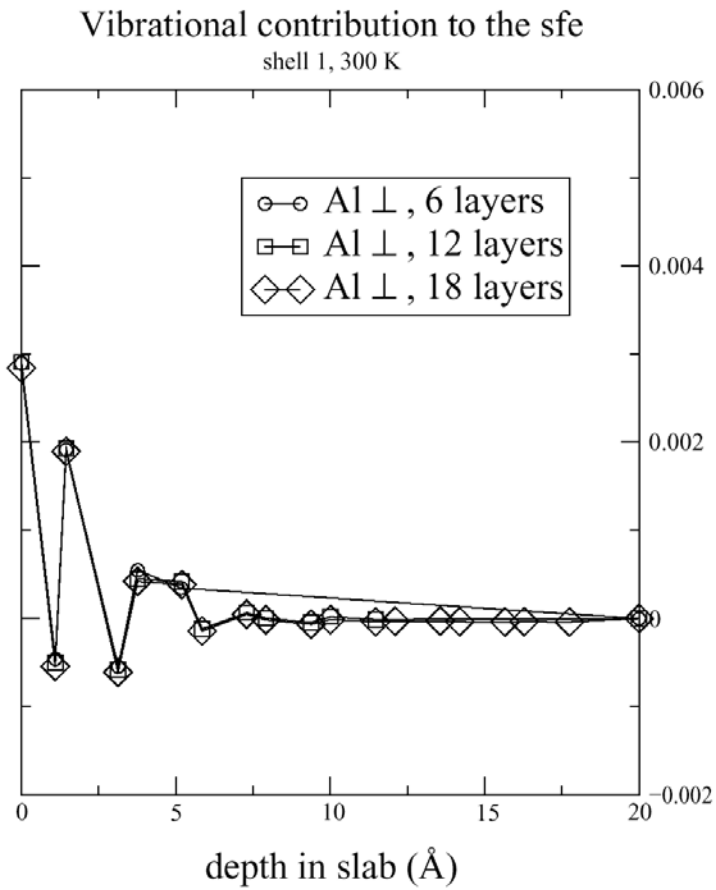
$$F(V,T) = E(V) + \sum_{\mathbf{q},j} \tfrac{1}{2} h\nu_j(q) + kT \ln[1 - \exp(-h\nu_j(q)/kT)]$$

Energy of static lattice at volume V

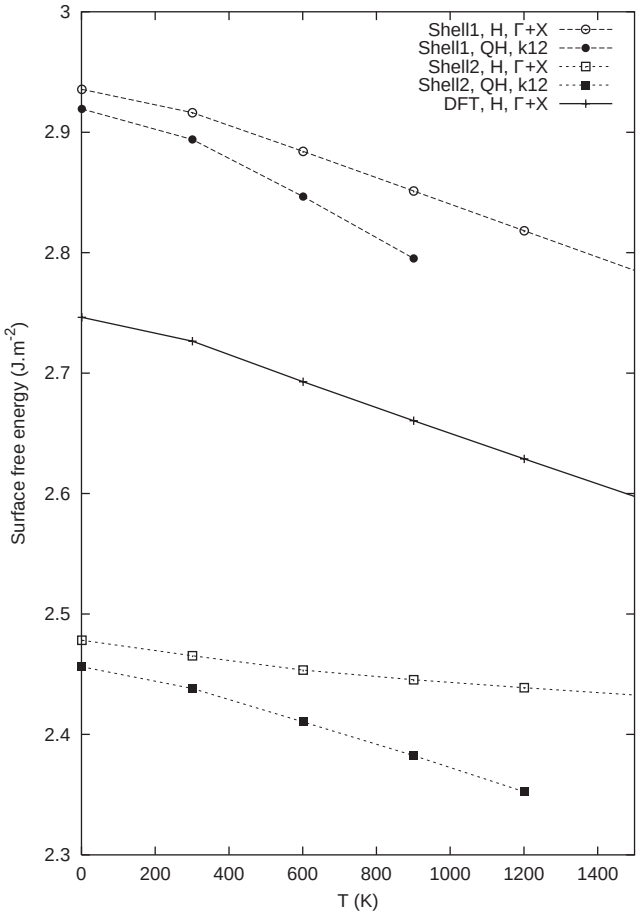
Surface mode



Layer-by-layer contributions to vibrational surface free energy



Surface free energies: Shell models and DFT



Conclusions

There is a first-principles scheme for calculation of excess surface and interface free energies σ which:

- includes handling excess of components like oxygen in terms of their partial pressure
- includes vibrational entropy

For alumina:

- Al terminated stoichiometric surface stable over most of oxygen pressure range < 1 atmosphere
- Large inward relaxation of Al consistently predicted (70-80%). Experiment gives ca. 50%…..?
- Adequate sampling with 2 phonon k-points
- Ab-initio harmonic: T-dependence of free energy similar to shell model
- Quasiharmonic or better approx. needed for quantitative accuracy (+/- 100mJm^{-2} at 1000K)

Thank you for your attention!

CMMP2003
6-9 April

http://www.qub.ac.uk/mp/con/cmmp2003/

http://physics.iop.org/IOP/Confs/CMMP2003/CMMP03.htm