Free metal and metal-oxide clusters: beyond the static, monostructure description

Luca M. Ghiringhelli
Fritz Haber Institute of the Max Planck Society, Berlin

CECAM/Psi-k Research Conference:
Multi-scale Modeling from First-Principles

Platja d'Aro, Spain, September 08-13, 2013

The big picture

Materials under operative conditions.
E.g., catalysts for heterogeneous catalysis

The widespread description and modeling of heterogeneous catalysis got stuck in the concepts and methods of the last century.

Most (nearly all) catalysis researchers focus on energies and energy barriers, however free energy and kinetics are also important.

A catalyst is usually not working efficiently from the very moment that the process starts, but a macroscopic “induction period” must rather elapse.

The catalytically active phase may exist only in a narrow range of the external conditions.

The big picture

Materials under operative conditions.
E.g., catalysts for heterogeneous catalysis

Not only the surface composition but also surface morphology can change in the course of a catalytic process.

Nanostructures of various shapes, point defects, extended defects such as steps, dislocations, and stacking faults, can result from and will be modified by interaction of the surface with the reactive environment.

The difference between “real-life catalysis” and “UHV surface chemical reactions” reflects the so-called “materials” and “pressure gap”.

A catalyst will never be the pristine material that is initially introduced in the reactor.

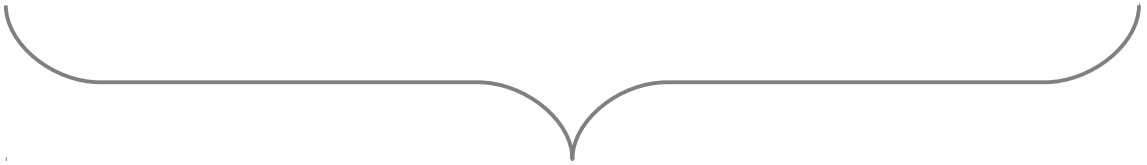
Road map

System as collection of
well separated minima:

Ab initio
atomistic thermodynamics

System in a fluxional
or liquid state:

Ab initio
Replica exchange
molecular dynamics

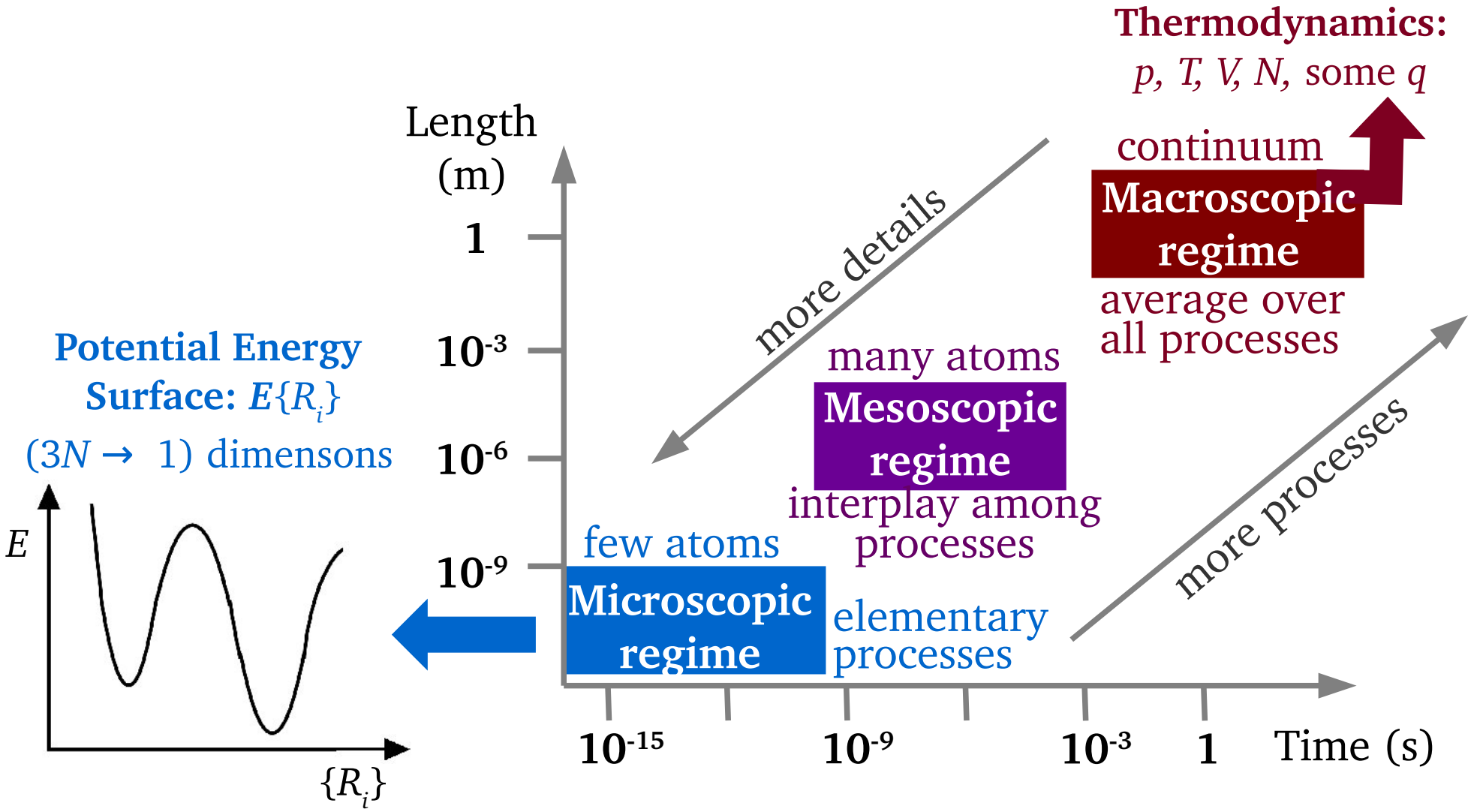


Validation of the total-energy method
(accuracy of the potential-energy surface)

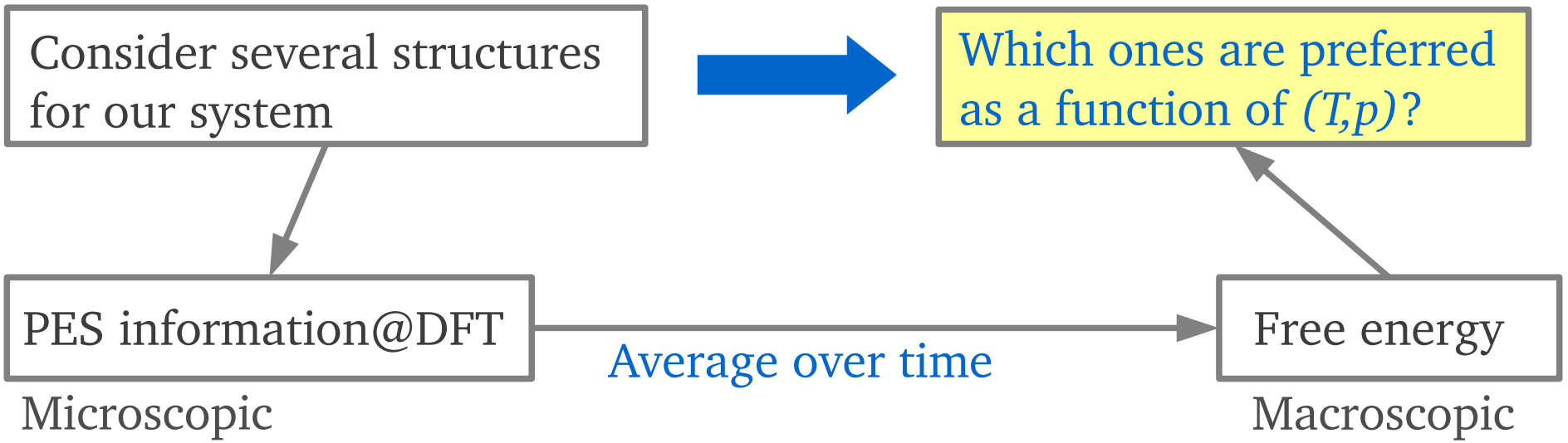
System as collection of
well separated minima:

Ab initio
atomistic thermodynamics

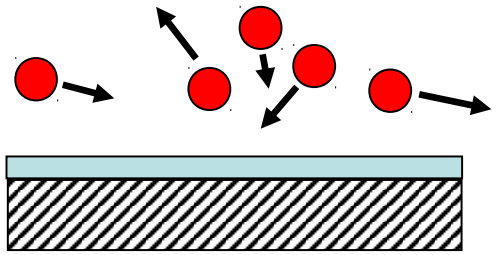
Extending the scale



Ab initio atomistic thermodynamics



A surface is coupled to the gas (or liquid) above it



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

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

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

Ab initio atomistic thermodynamics

Showcase: Mg clusters in oxygen (-containing) atmosphere

Formation free energy — Free energy of pristine surface/cluster

$$\Delta G_f(T, p_{O_2}) = F_{Mg_M O_x}(T) - F_{Mg_M}(T) - x\mu_O(T, p_{O_2})$$

Free energy of surface/cluster + ligand — Chemical potential of ligand

$$F(T) = \underbrace{F^{Tr}(T) + F^{Rot}(T) + F^{Vib}(T)}_{\text{Trans, Rot. \& vibs. free energy}} + \underbrace{F^{Symm}(T) + F^{Spin}(T)}_{\text{symmetry \& spin contribution}} + E^{DFT}$$

C.M. Weinert and M.Scheffler, Mat. Sci. Forum 10-12, 25 (1986).
K. Reuter, C. Stampfl, and M.S., in: Handbook of Materials Modeling, Vol. 1. (Ed. Sid Yip), Springer 2005.
R. Fowler and E.A. Guggenheim, Statistical thermodynamics (Cambridge Press, Cambridge, 1949)

Which structures? Unbiased search: *cascade* genetic algorithm

A
- random initial pool; care for including diversity
- local geometry optimization with classical force field (e.g., reaxFF [1])
- evaluation of the *fitness* function
- selection of two parents, crossover, mutation

Why? Creation of a "pre-digested" initial pool for DFT-based GA

B
- initial pool from previous step
- local geometry optimization @ PBE+vdW / light settings;
- structure recognition, early rejection if "similar" to known structure.
- in cascade, local geometry optimization @ PBE+vdW / tight settings
- structure recognition, rejection if "similar" to known structure.
- energy evaluation with PBE0+vdW; evaluation of the fitness function
- selection of two parents, crossover, mutation

Parallel version: all replicas draw initial structures from a common pool and update the common pool.
- no idling time: perfectly linearly scaling parallelization.

[1] A. van Duin *et al.*, J. Chem. Phys. A **105**, 9396 (2001); Q. Zhang *et al.*, Phys. Rev. B **69**, 045423 (2004)

Ab initio atomistic thermodynamics

Showcase: Mg clusters in oxygen (-containing) atmosphere

Formation free energy — Free energy of pristine surface/cluster

$$\Delta G_f(T, p_{O_2}) = F_{Mg_M O_x}(T) - F_{Mg_M}(T) - x\mu_O(T, p_{O_2})$$

Free energy of surface/cluster + ligand — Chemical potential of ligand

$$F(T) = \underbrace{F^{Tr}(T) + F^{Rot}(T) + F^{Vib}(T)}_{\text{Trans, Rot. \& vibs. free energy}} + \underbrace{F^{Symm}(T) + F^{Spin}(T)}_{\text{symmetry \& spin contribution}} + E^{DFT}$$

C.M. Weinert and M.Scheffler, Mat. Sci. Forum 10-12, 25 (1986).
K. Reuter, C. Stampfl, and M.S., in: Handbook of Materials Modeling, Vol. 1. (Ed. Sid Yip), Springer 2005.
R. Fowler and E.A. Guggenheim, Statistical thermodynamics (Cambridge Press, Cambridge, 1949)

Free energy? Harmonic, beyond, and further beyond

- Disjointed minima, harmonic PES (low T): analytic expression

$$\sum_{i=1}^{M}\left[\frac{\hbar\omega_i}{2}+k_{\mathrm{B}}T\ln\left(1-\exp\left(\frac{\hbar\omega_i}{k_{\mathrm{B}}T}\right)\right)\right]$$

→ Input: evaluation of harmonic spectrum

- Disjointed minima, non-harmonic PES (higher T):

Total energy | Potential energy | Kinetic energy

$$\frac{\partial[\beta F(\beta)]}{\partial\beta}=\langle E\rangle_\beta=\langle U\rangle_\beta+\frac{N}{2\beta}$$

→ Input: from NVT molecular dynamics

DFT total energy of 0K structure | Harmonic F

$$\beta F(\beta) = \beta U^{\mathrm{ref}}+\beta F^{\mathrm{vib}}(\beta)+\int_{\beta_0}^{\beta}d\beta(\langle U\rangle_\beta-U^{\mathrm{ref}}-\frac{N}{2\beta})$$

Free energy? Harmonic, beyond, and further beyond

- Disjointed minima, harmonic PES (low T): analytic expression

$$\sum_{i=1}^{M}\left[\frac{\hbar\omega_i}{2}+k_{\mathrm{B}}T\ln\left(1-\exp\left(\frac{\hbar\omega_i}{k_{\mathrm{B}}T}\right)\right)\right]$$

→ Input: evaluation of harmonic spectrum

- Disjointed minima, non-harmonic PES (higher T):

It works only if
- there is only one reference structure and
- the integration path is reversible

$$\beta F(\beta) = \beta U^{\mathrm{ref}} + \beta F^{\mathrm{vib}}(\beta) + \int_{\beta_0} d\beta(\langle U\rangle_\beta - U^{\mathrm{ref}} - \frac{N}{2\beta})$$

- Multiple minima: multi-canonical methods, replica exchange

Ab initio atomistic thermodynamics

Showcase: Mg clusters in oxygen (-containing) atmosphere

Formation free energy — Free energy of pristine surface/cluster

$$\Delta G_f(T, p_{O_2}) = F_{Mg_M O_x}(T) - F_{Mg_M}(T) - x\,\mu_O(T, p_{O_2})$$

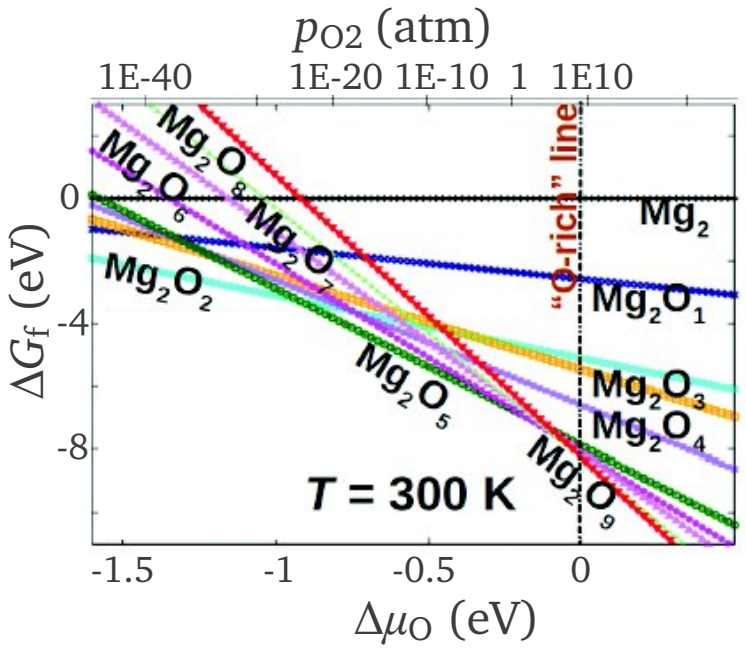
Free energy of surface/cluster + ligand — Chemical potential of ligand

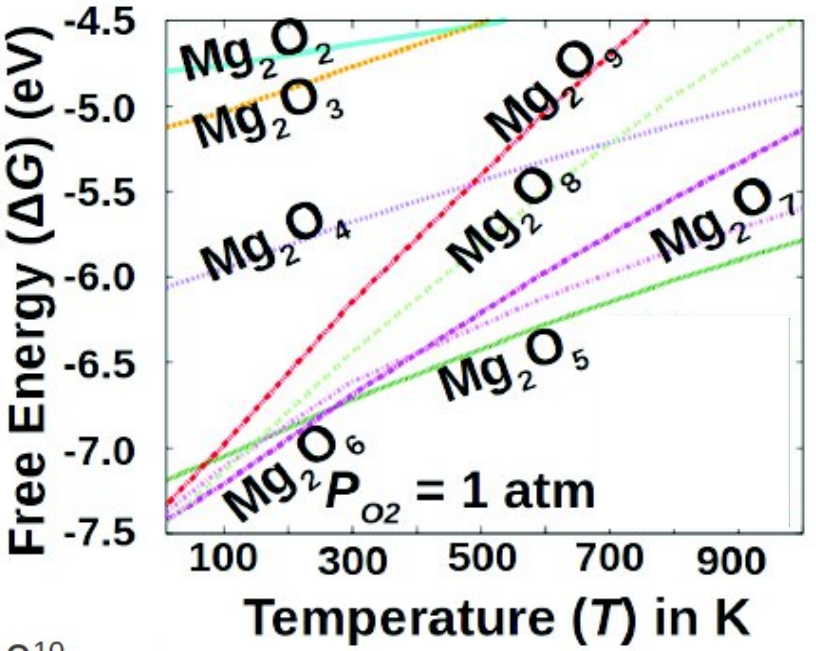
$$\mu_O(T,p) = \tfrac{1}{2}\,\mu_{O_2}(T,p_0) + \tfrac{1}{2}\,kT \ln (p/p_0)$$

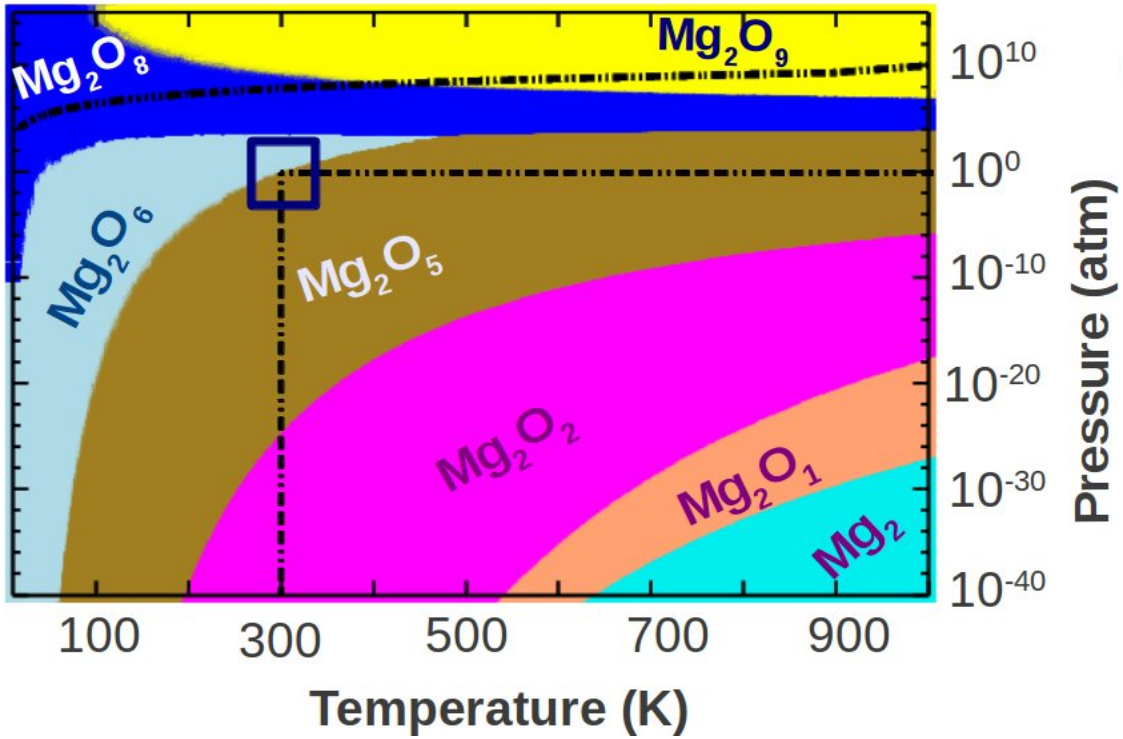
$$F(T) = \underbrace{F^{Tr}(T) + F^{Rot}(T) + F^{Vib}(T)}_{\text{Trans, Rot. \& vibs. free energy}} + \underbrace{F^{Symm}(T) + F^{Spin}(T)}_{\text{symmetry \& spin contribution}} + E^{DFT}$$

C.M. Weinert and M.Scheffler, Mat. Sci. Forum 10-12, 25 (1986).
K. Reuter, C. Stampfl, and M.S., in: Handbook of Materials Modeling, Vol. 1. (Ed. Sid Yip), Springer 2005.
R. Fowler and E.A. Guggenheim, Statistical thermodynamics (Cambridge Press, Cambridge, 1949)

Ab initio atomistic thermodynamics: phase diagrams





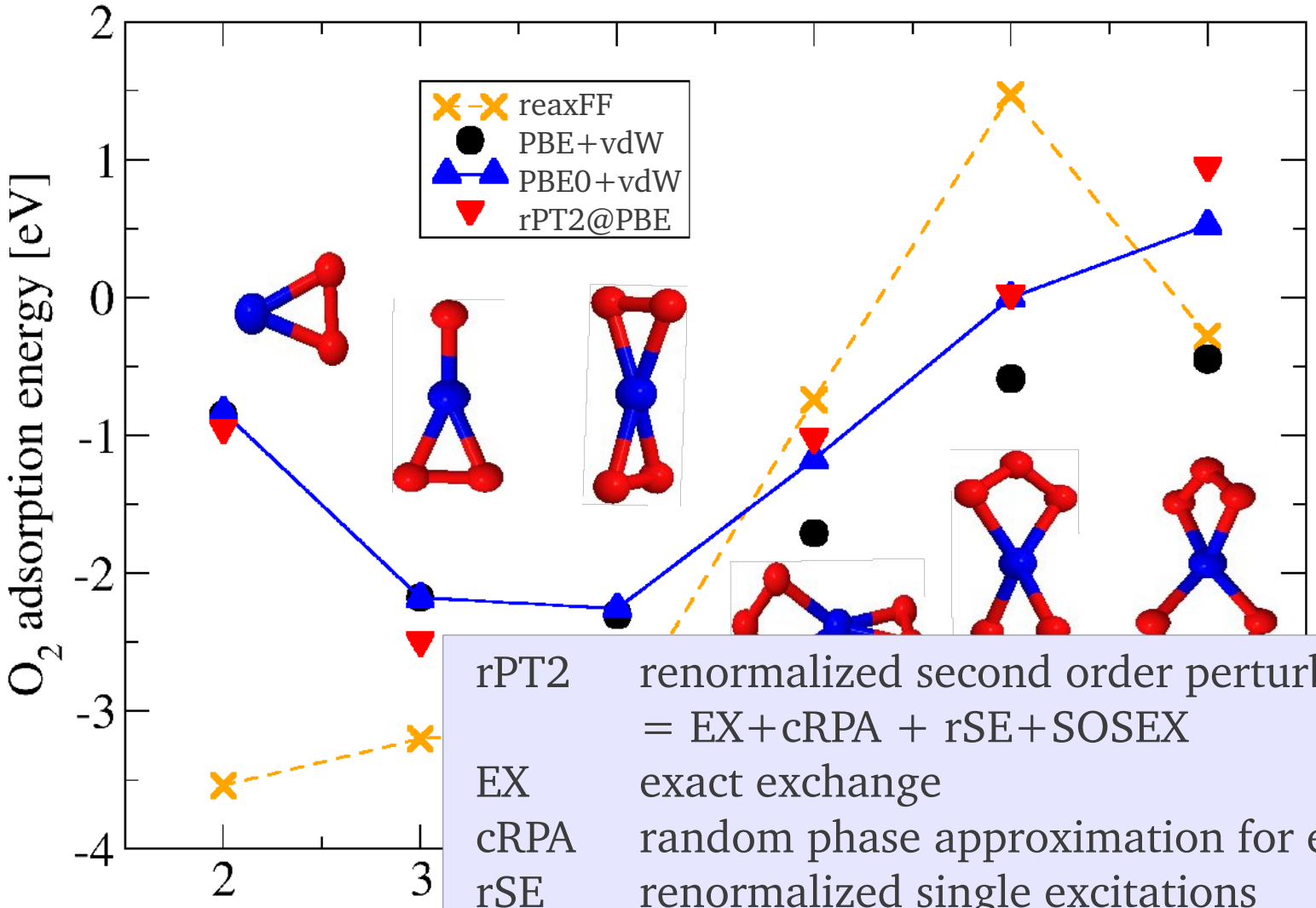


Validation of the total-energy method (accuracy of the potential energy surface)

Case study one: reaxFF vs DFT for Mg_MO_x clusters

Case study two: out-of-water “bio” force fields vs DFT for gas phase poly-peptides

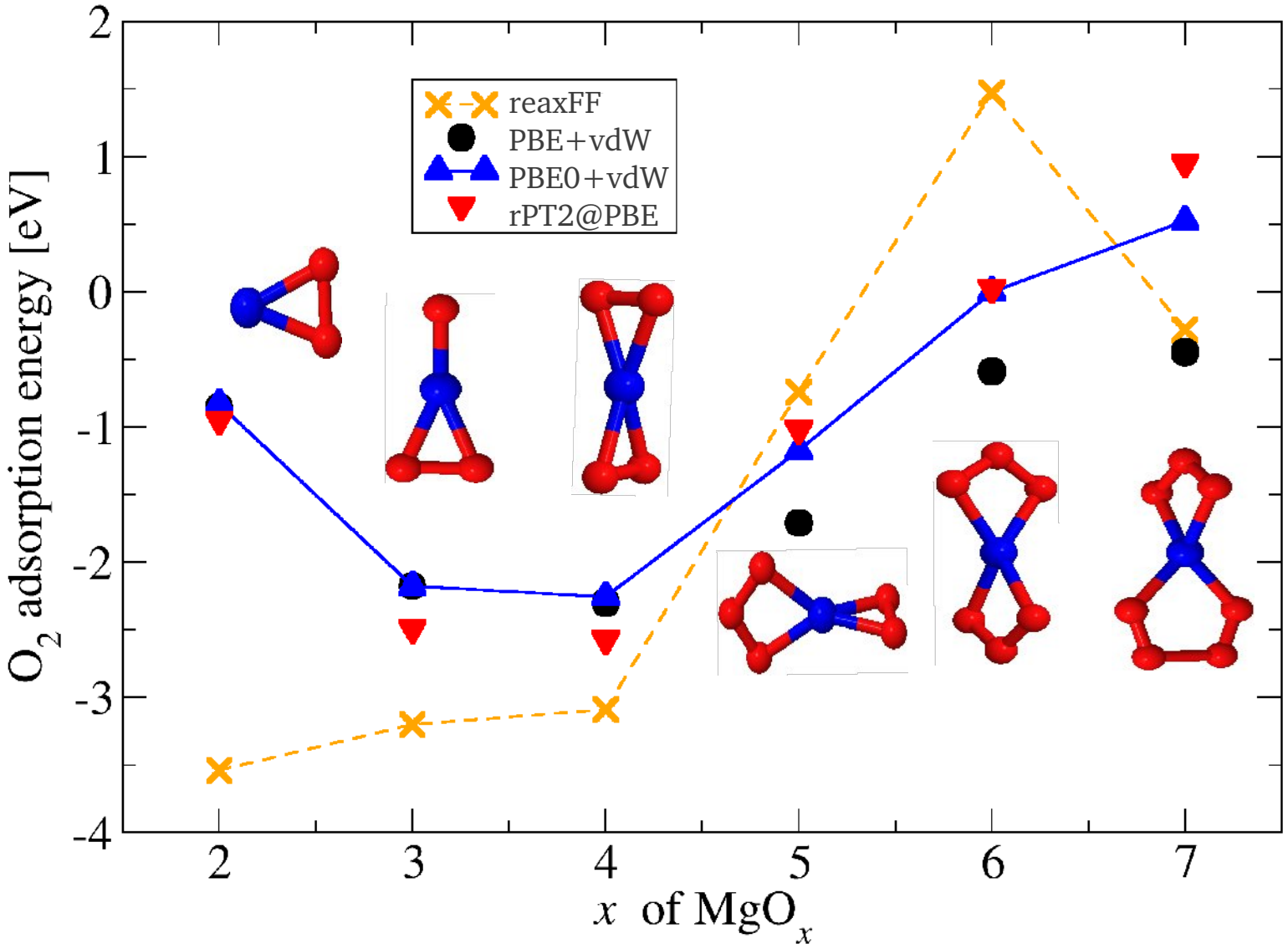
Case study one: reaxFF vs DFT for Mg_MO_x clusters



rPT2	renormalized second order perturbation theory = EX+cRPA + rSE+SOSEX
EX	exact exchange
cRPA	random phase approximation for e^- correlation
rSE	renormalized single excitations
SOSEX	second-order screened exchange

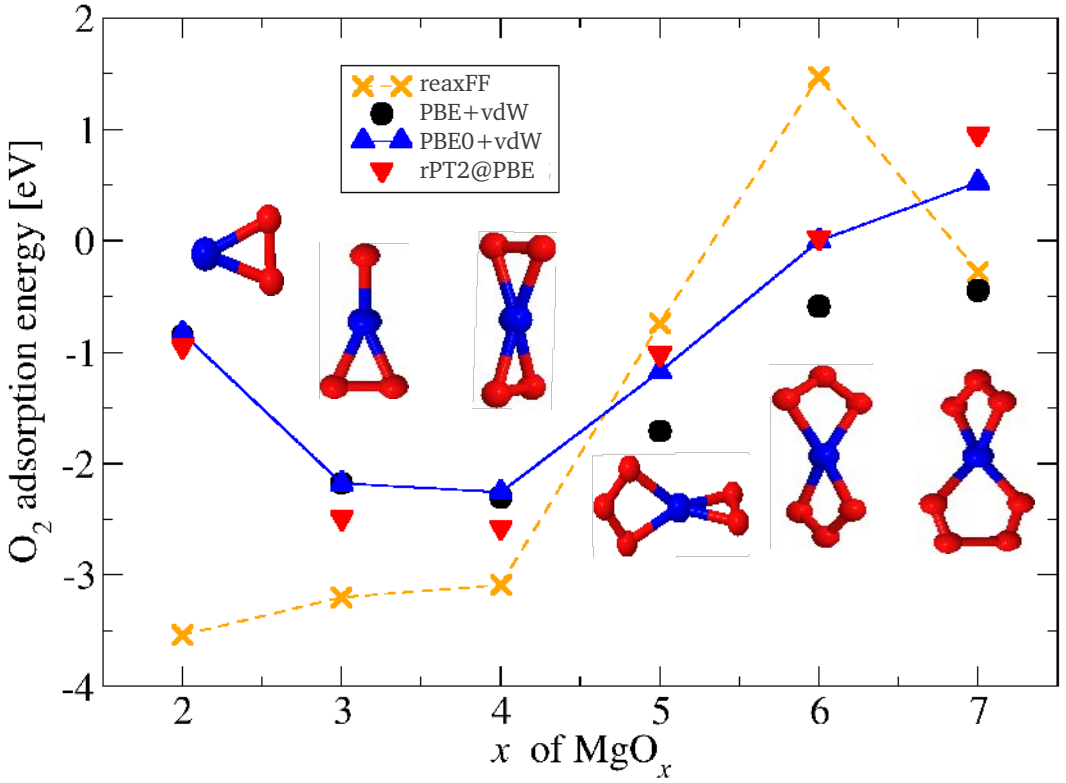
X. Ren, P. Rinke, C. Joas, and M. Scheffler, J. Mater. Sci. (2012)
X. Ren, P. Rinke, G.E. Scuseria, and M. Scheffler, PRB (2013)

Benchmarking GGA and hybrid functionals



PBE+vdW quality deteriorates with increasing O_2 coverage

Benchmarking GGA and hybrid functionals



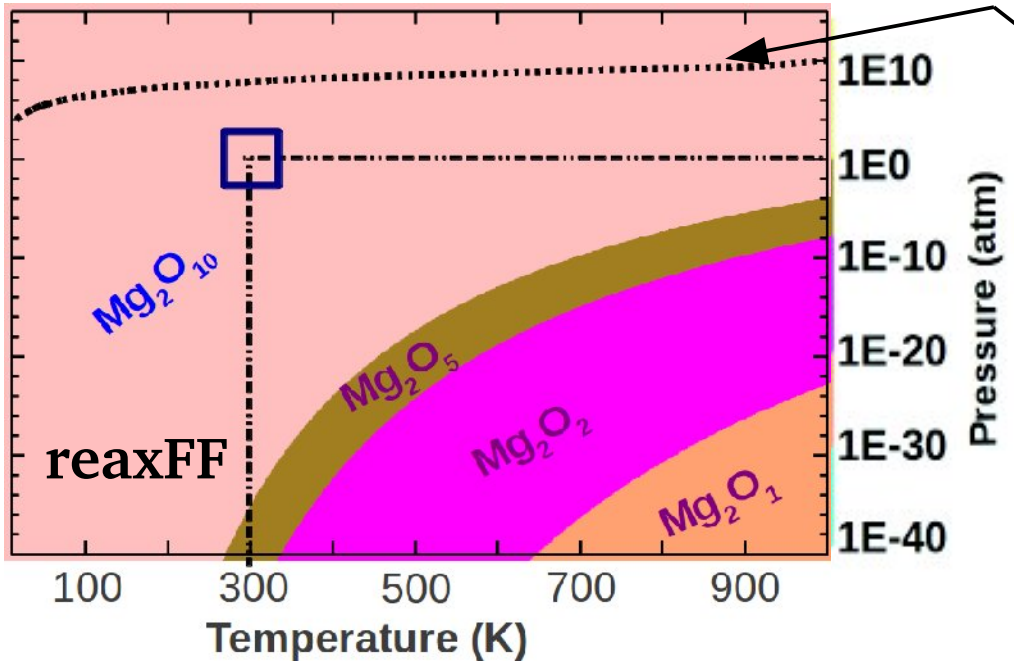
Among the (reactive) force fields designed for a wide class of elements, reaxFF is possibly the best.

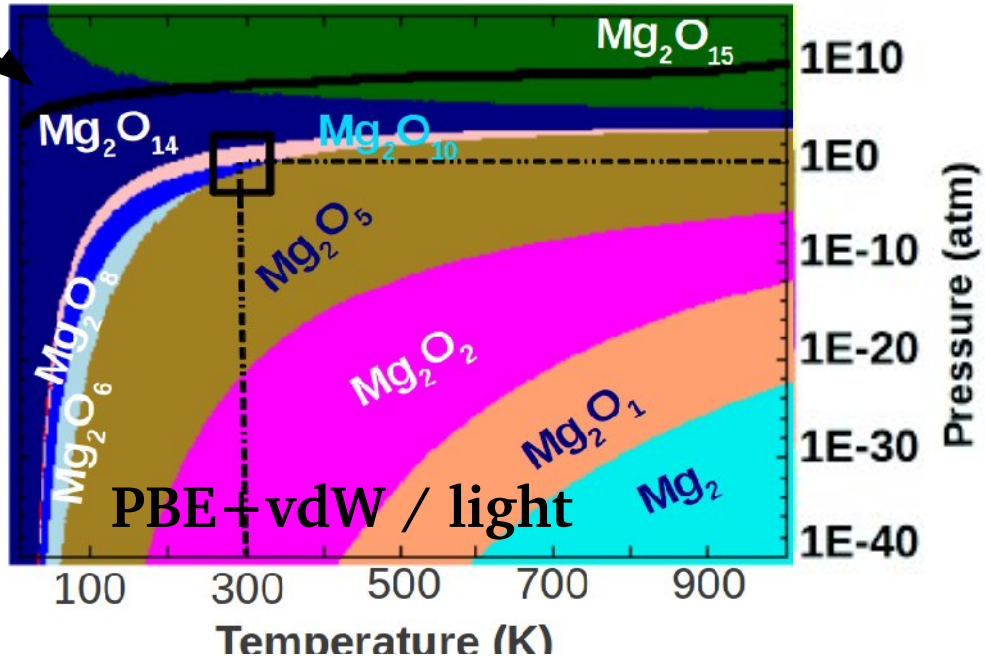
However the "range of validity" of the reaxFF is narrow and only covering those situations that were used to fit its parameters.

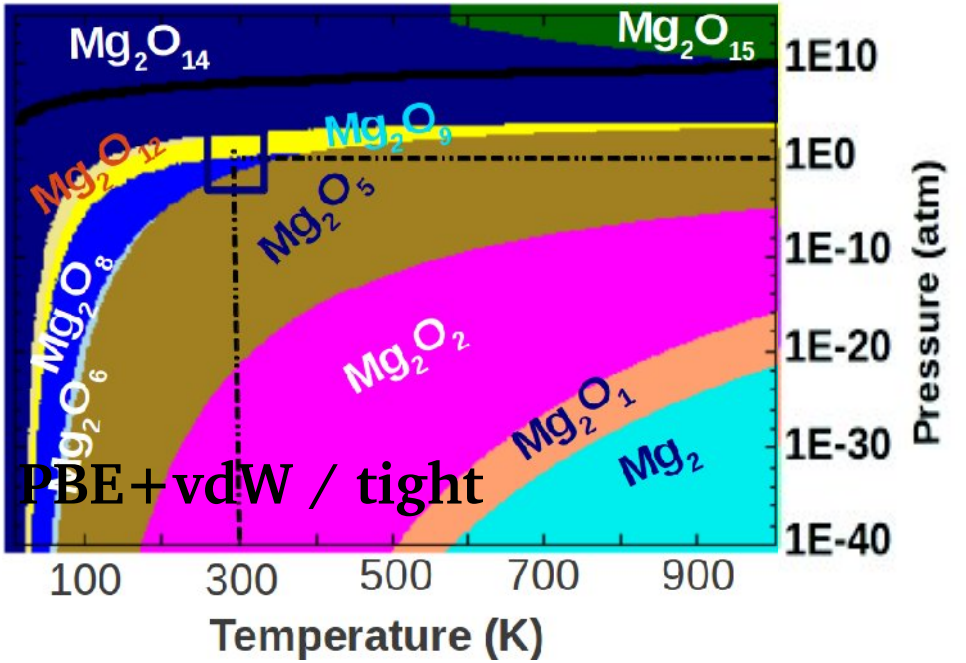
Information about the bulk and (some) surface situations are not sufficient for describing small clusters.

Benchmarking GGA and hybrid functionals

Condensation of oxygen droplets

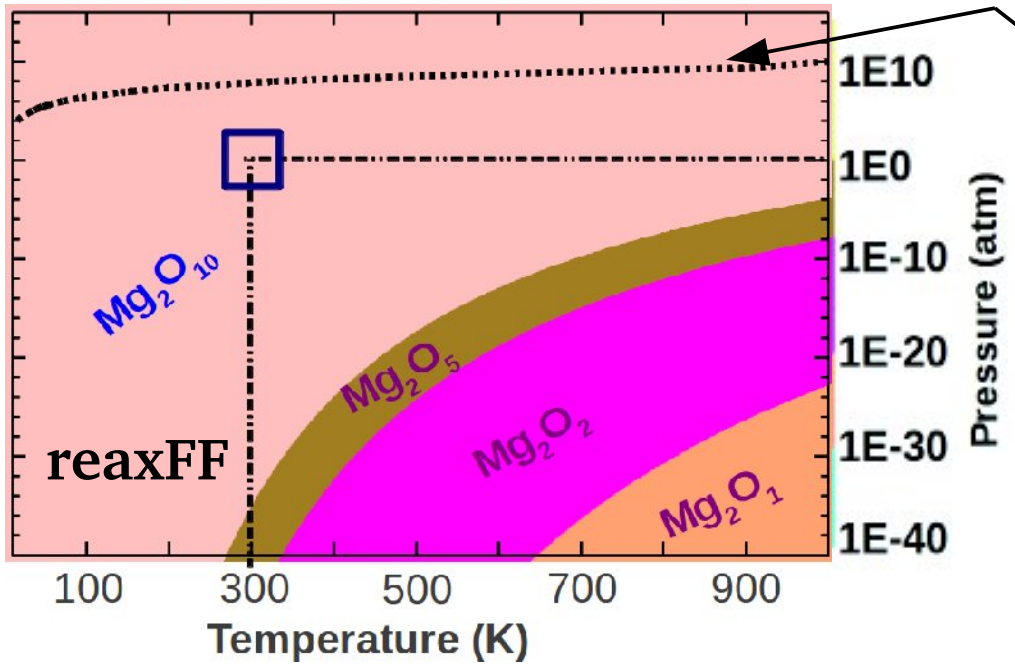


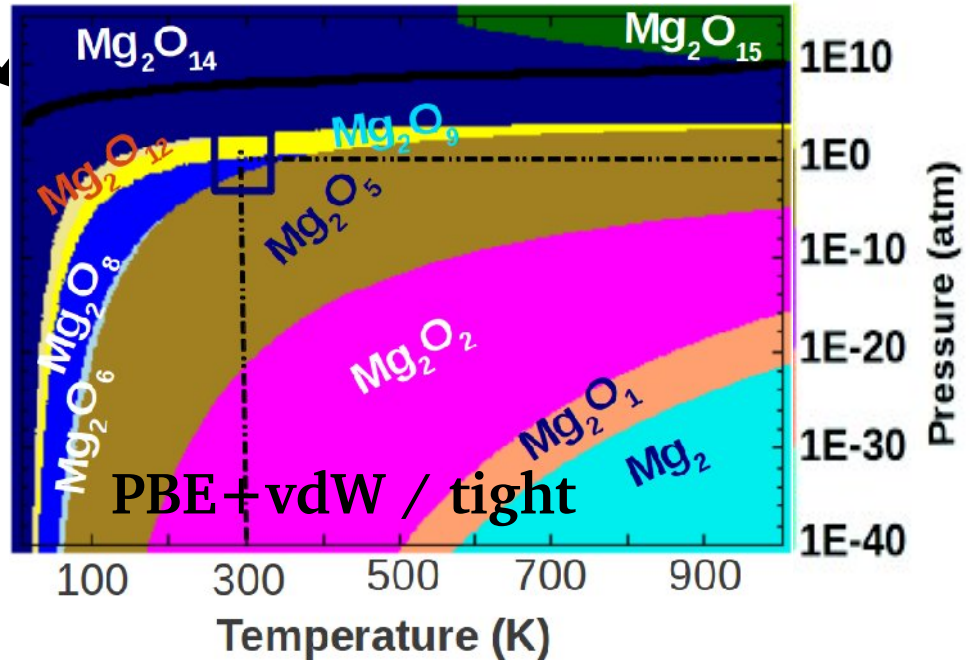




Benchmarking GGA and hybrid functionals

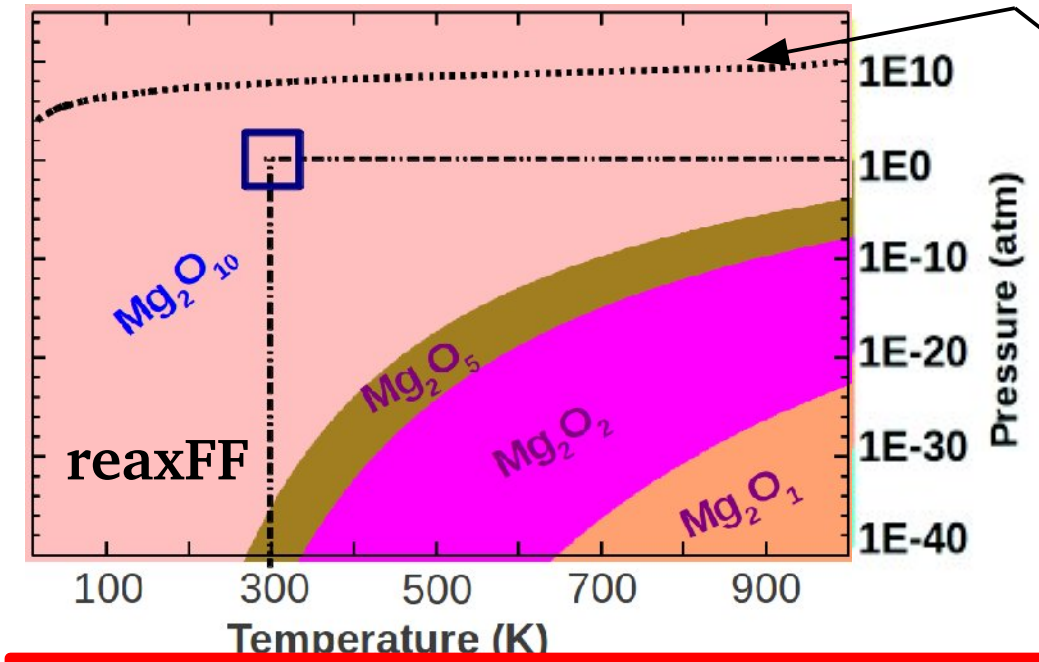
Condensation of oxygen droplets

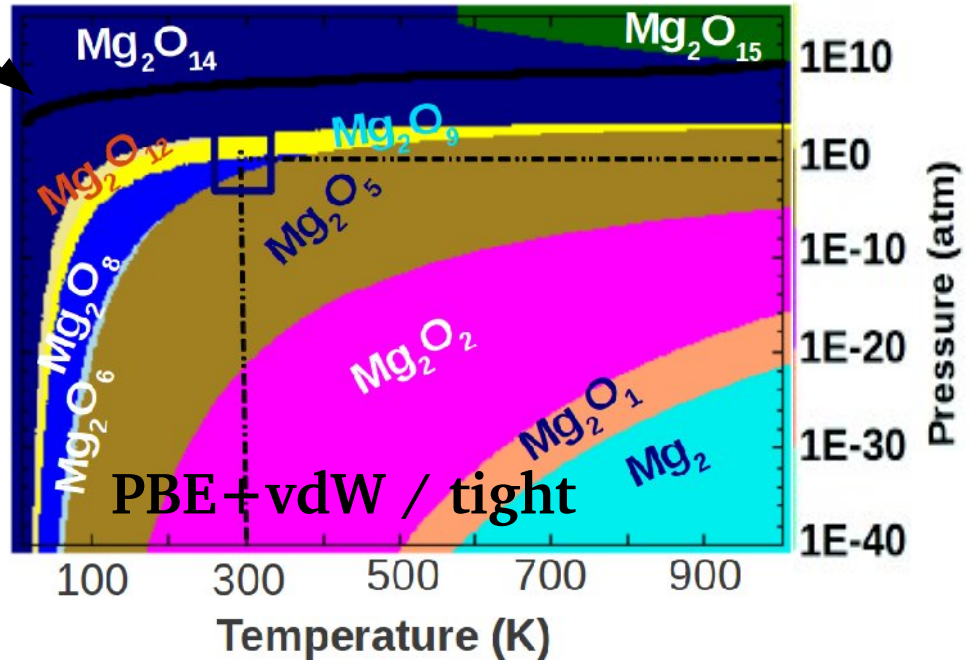


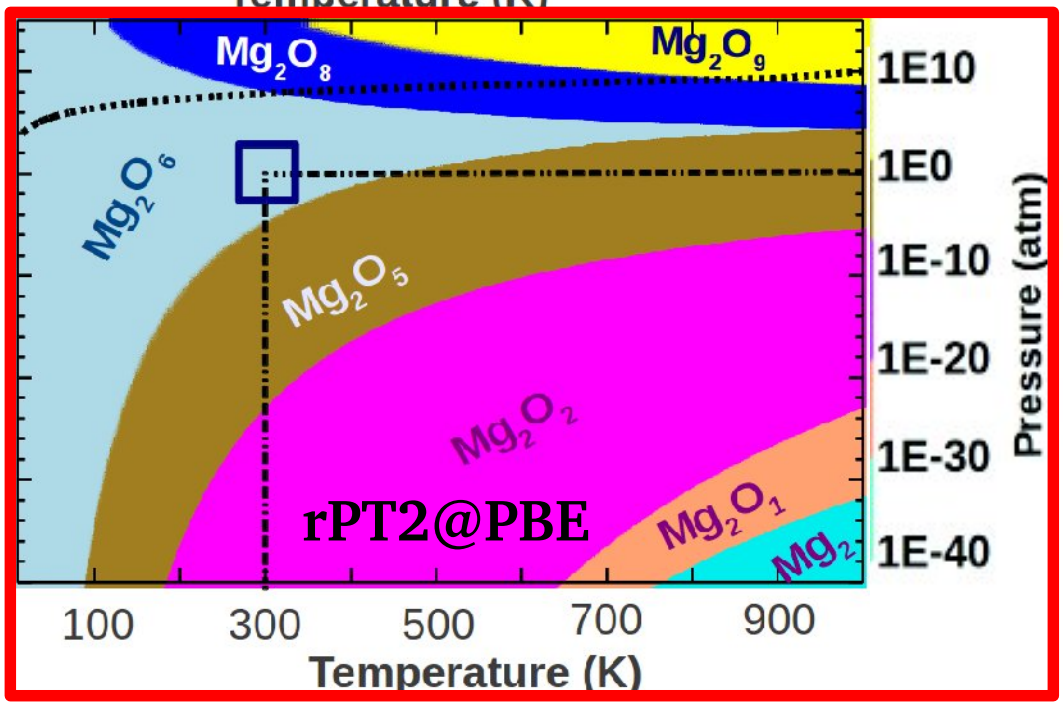


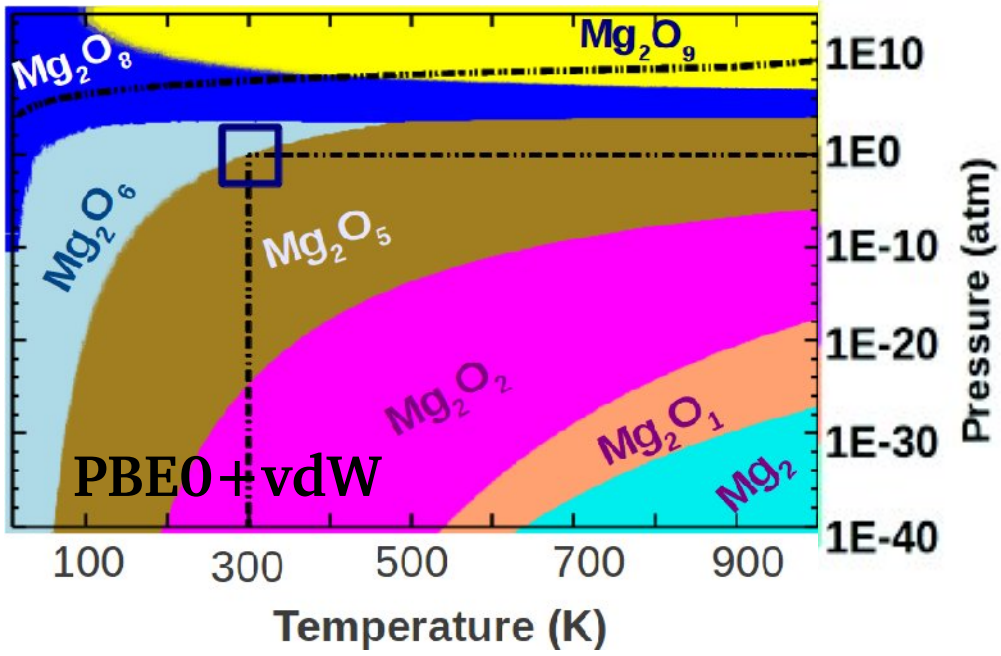
Benchmarking GGA and hybrid functionals

Condensation of oxygen droplets



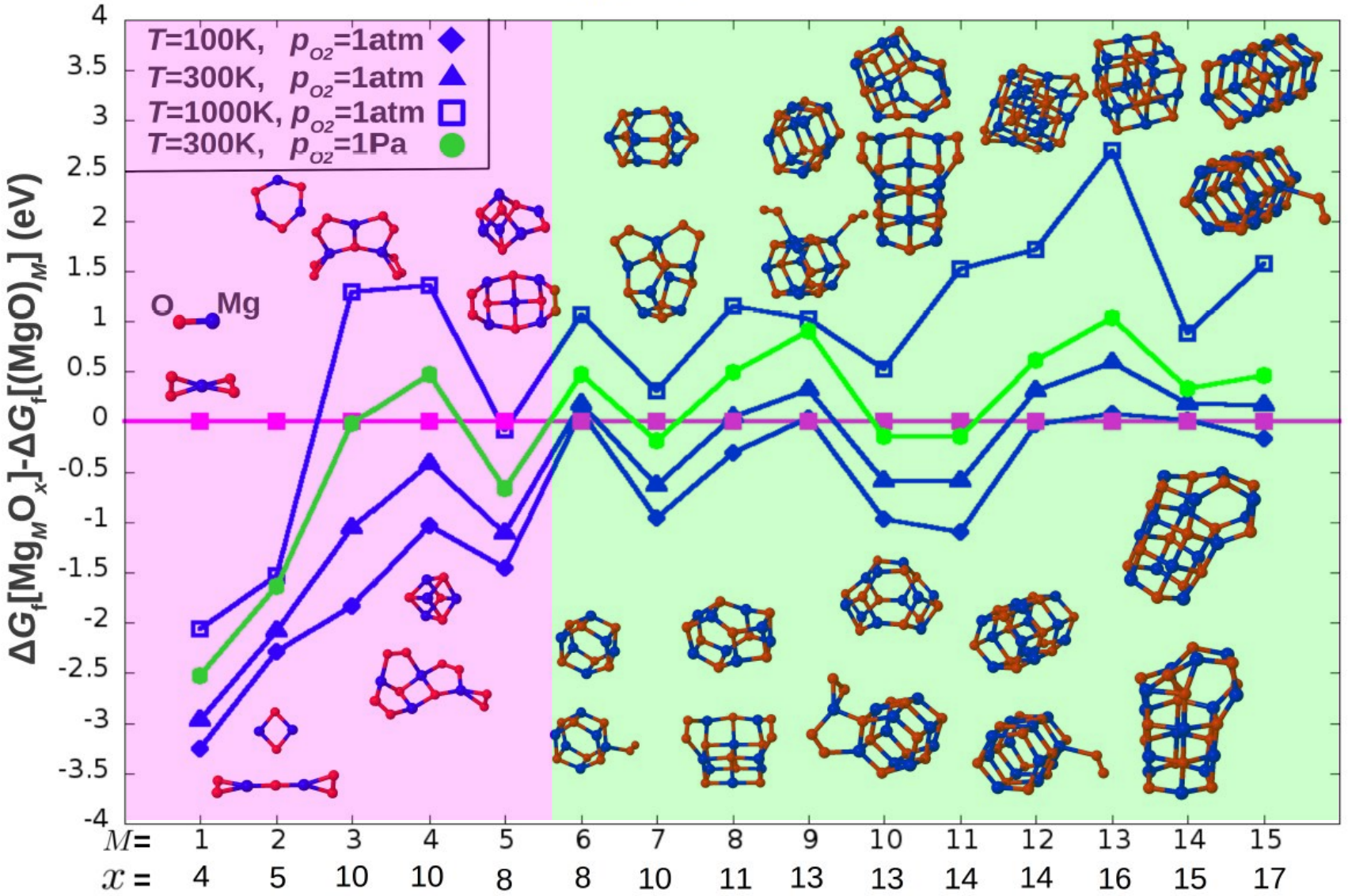






Thermodynamic stability of Mg_MO_x clusters

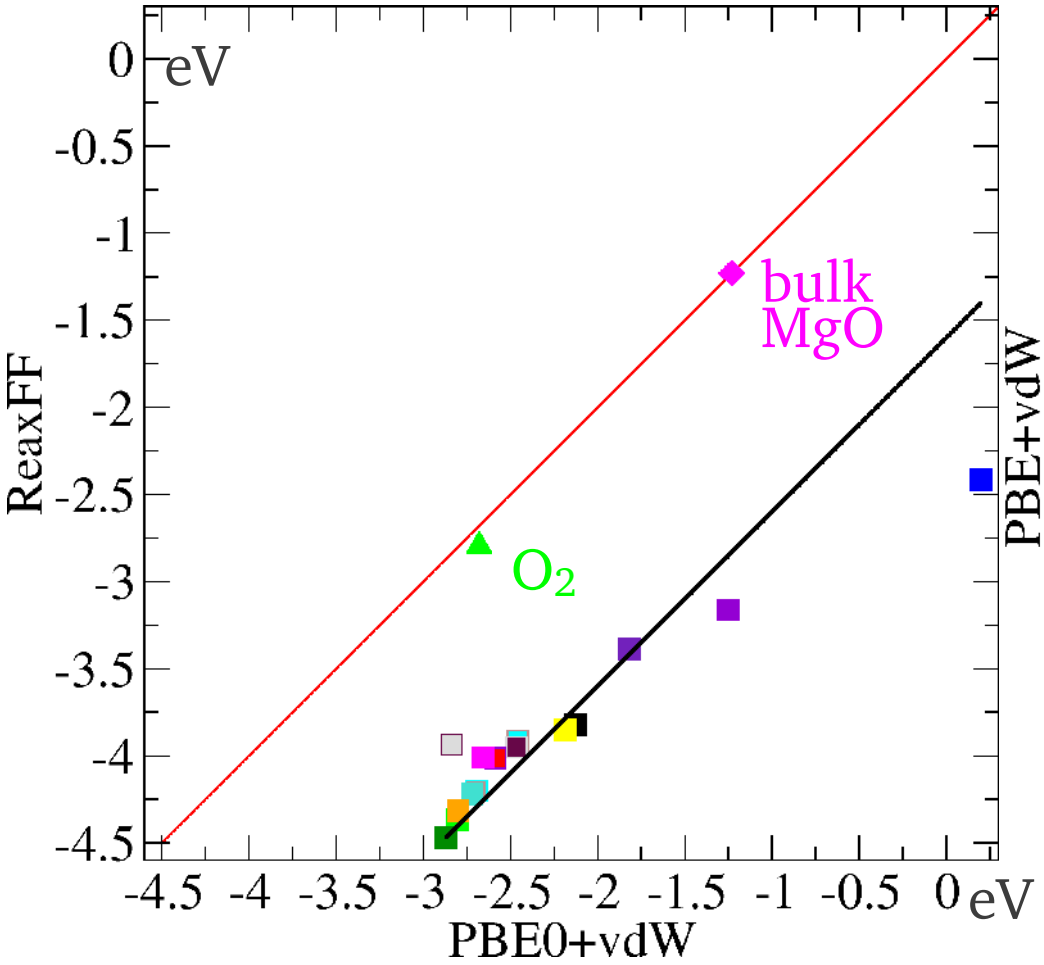
Non stoichiometric Competition / coexistence



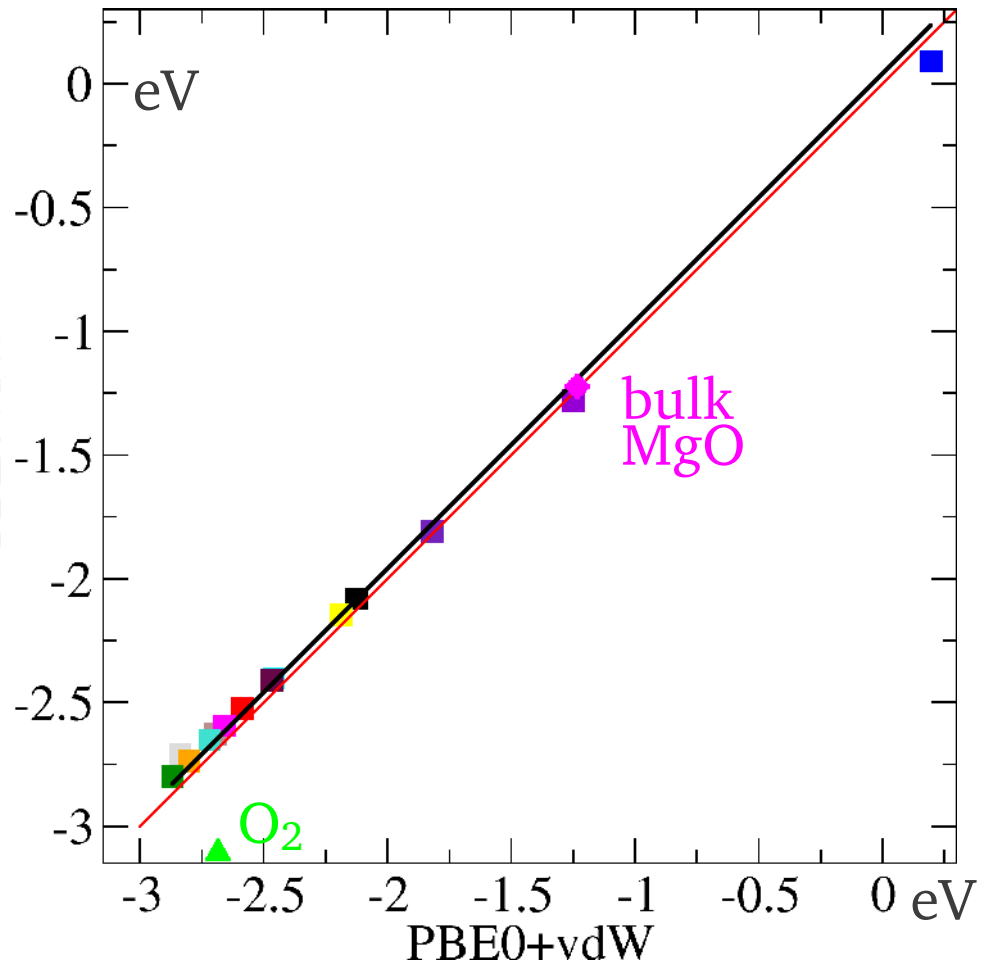
S. Bhattacharya, S. Levchenko, LMG, and M. Scheffler, PRL (2013)

Accuracy of a reactive force field vs DFT

Stochiometric $(MgO)_M$ clusters, global minima; $1 \leq M \leq 15$



Offset: -1.60 eV
MAE: 0.20 eV

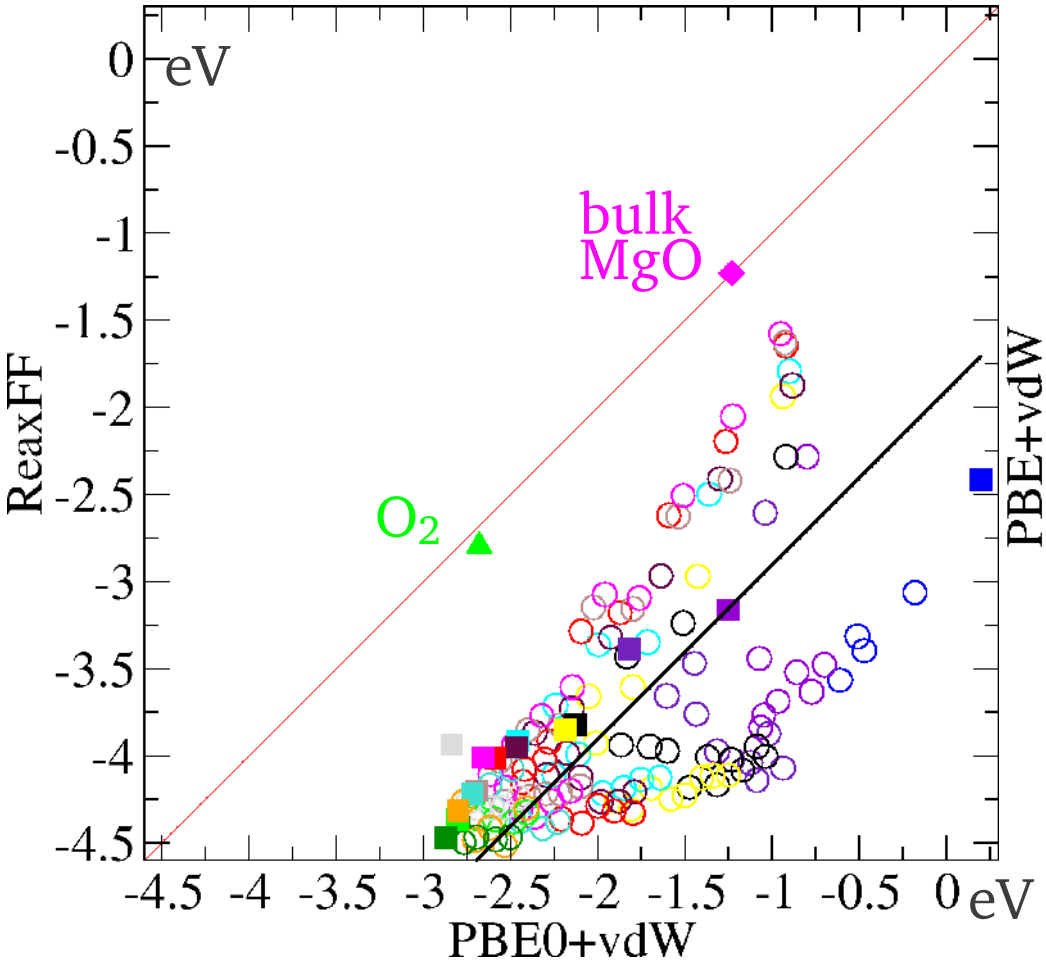


Offset: 0.04 eV
MAE: 0.04 eV

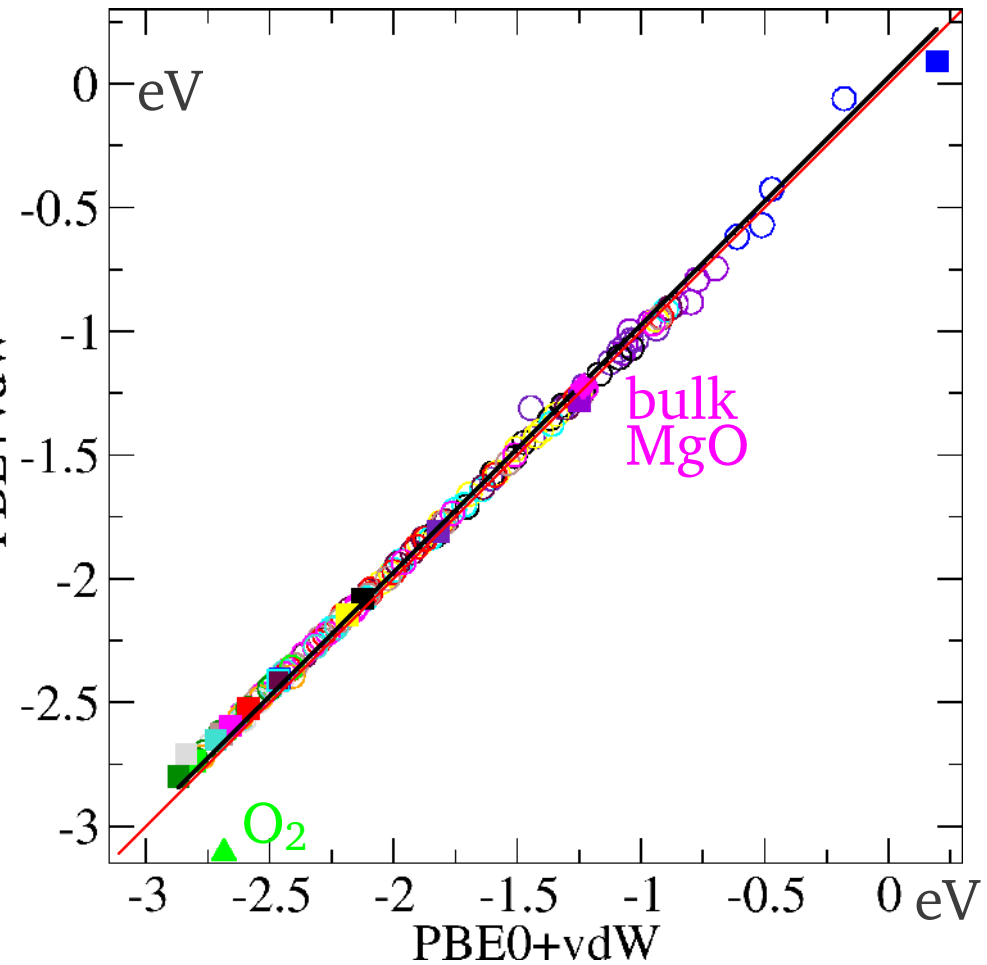
Cohesion/formation energy, referred to atomic Mg and half of O_2 total energy

Accuracy of a reactive force field vs DFT

Stochiometric + non-stochiometric Mg_MO_x clusters, global minima; $1 \leq M \leq 15$



Offset: -1.91 eV
MAE: 0.48 eV

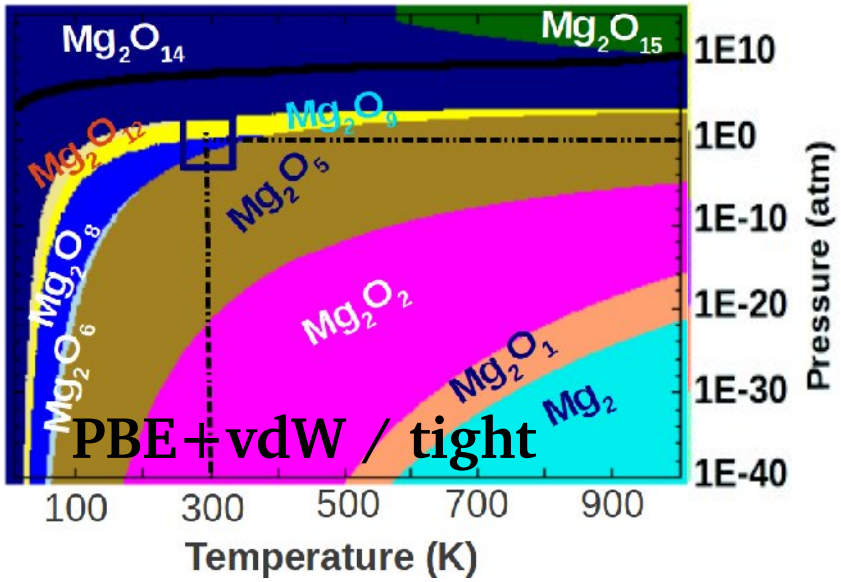


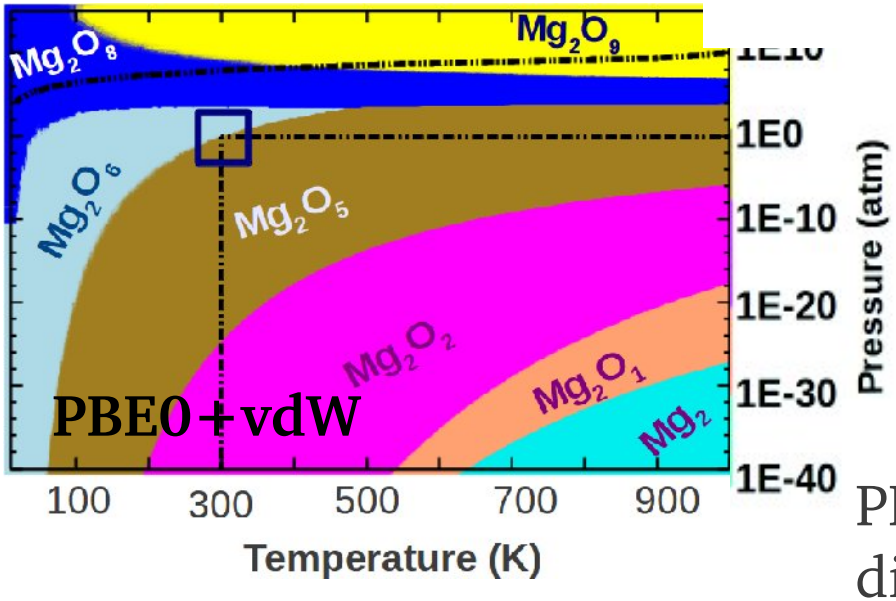
Offset: 0.03 eV
MAE: 0.03 eV

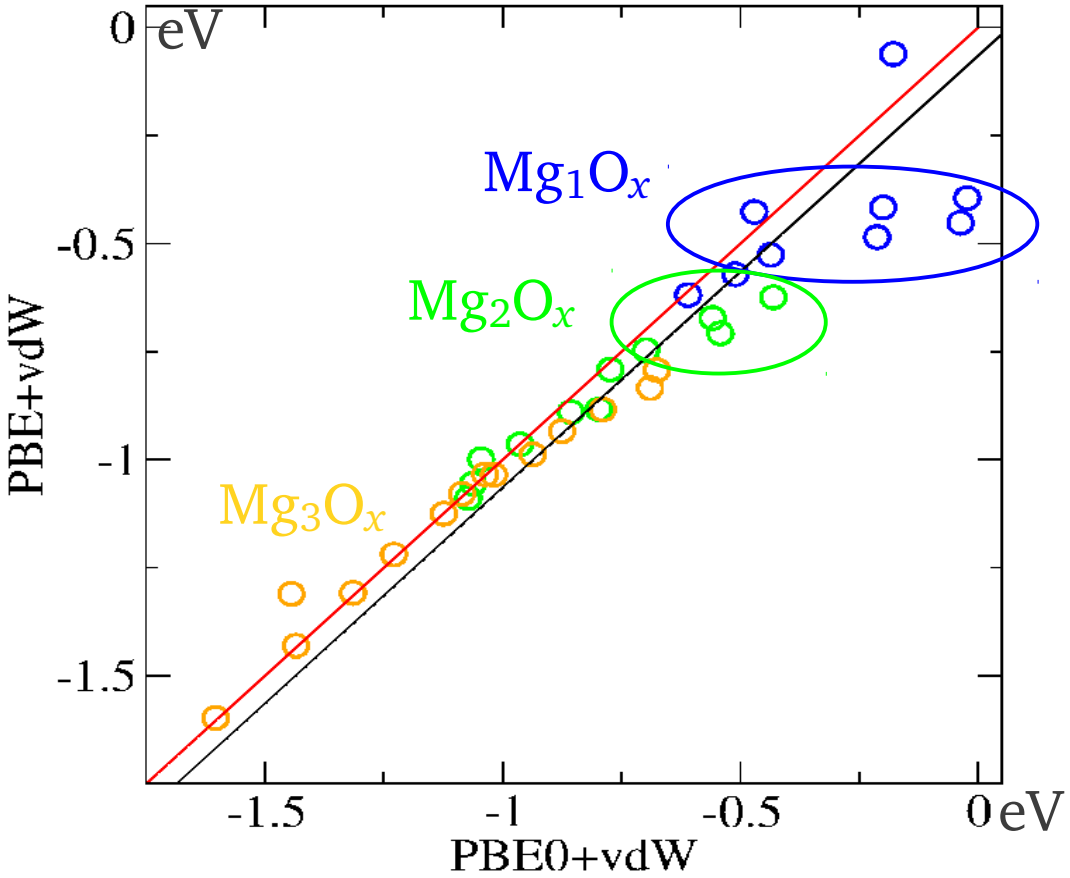
Cohesion/formation energy, referred to atomic Mg and half of O_2 total energy

Accuracy of a reactive force field vs DFT

Stochiometric + non-stochiometric Mg_MO_x clusters, global minima; $1 \le M \le 3$





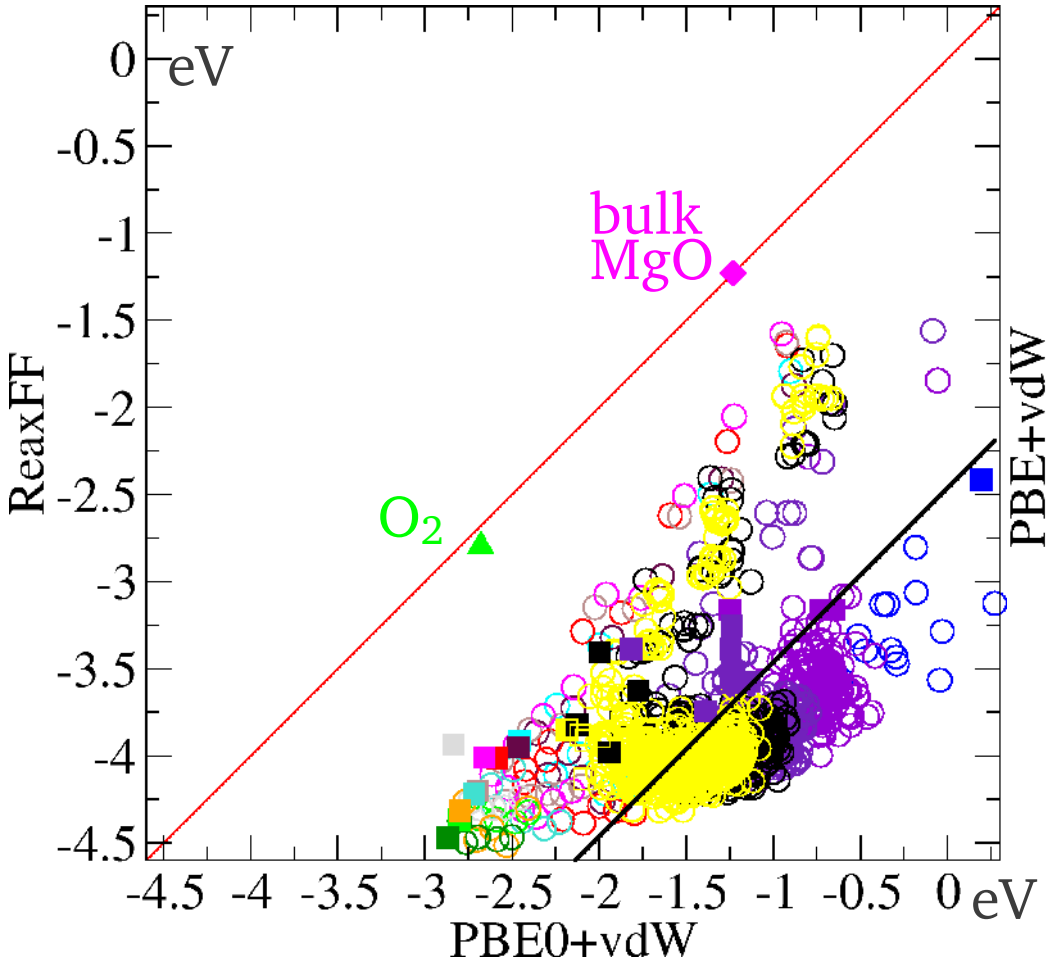


Offset: -0.07 eV
MAE: 0.09 eV

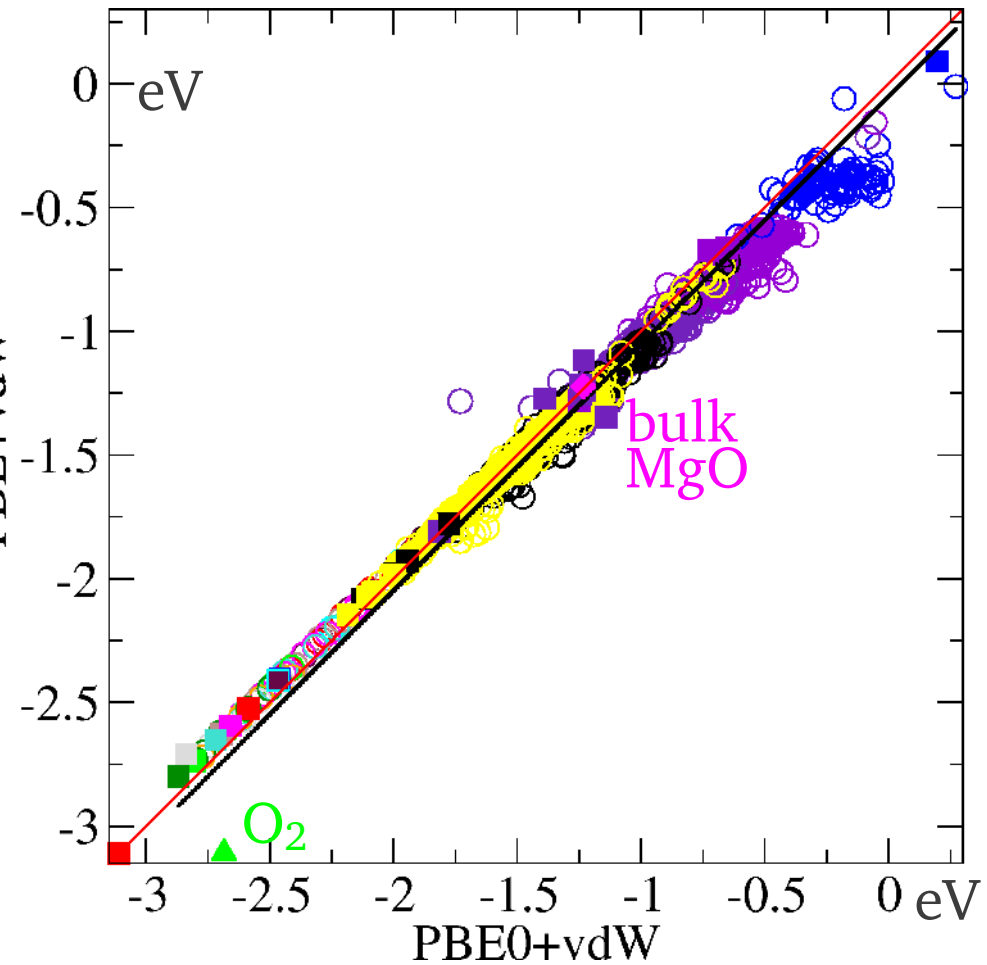
PBE+vdW favors high O-coverage: the phase diagram a higher p is totally unreliable

Accuracy of a reactive force field vs DFT

Stochiometric and non-stochiometric Mg_MO_x clusters, all isomers; $1 \leq M \leq 15$



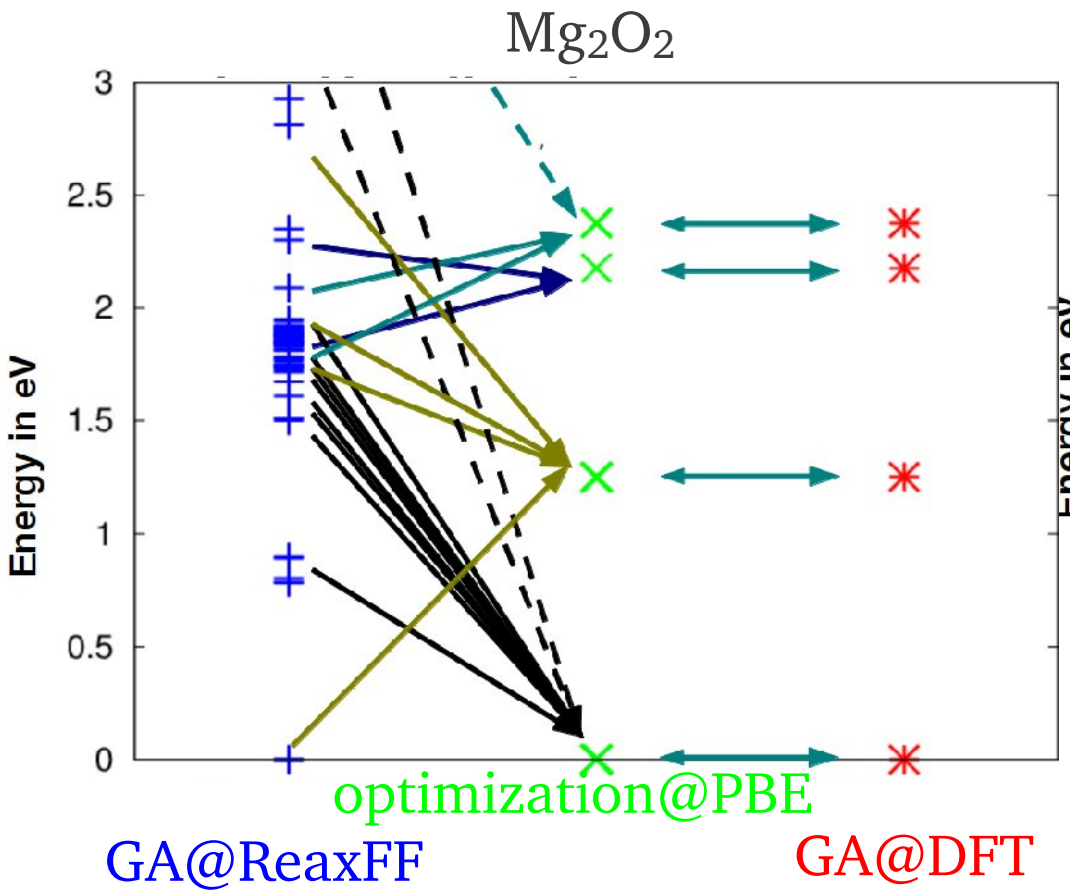
Offset: -2.46 eV
MAE: 0.38 eV

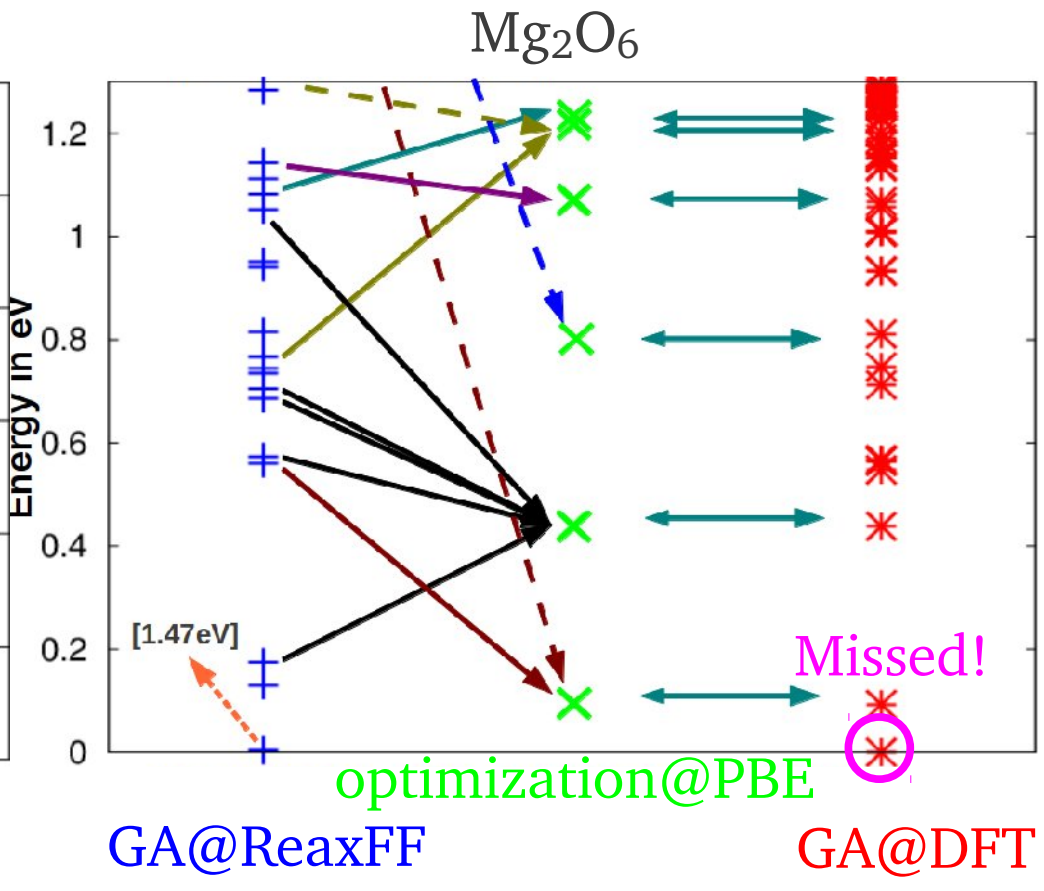


Offset: 0.05 eV
MAE: 0.05 eV

Cohesion/formation energy, referred to atomic Mg and half of O_2 total energy

DFT as post-production applied to force field?

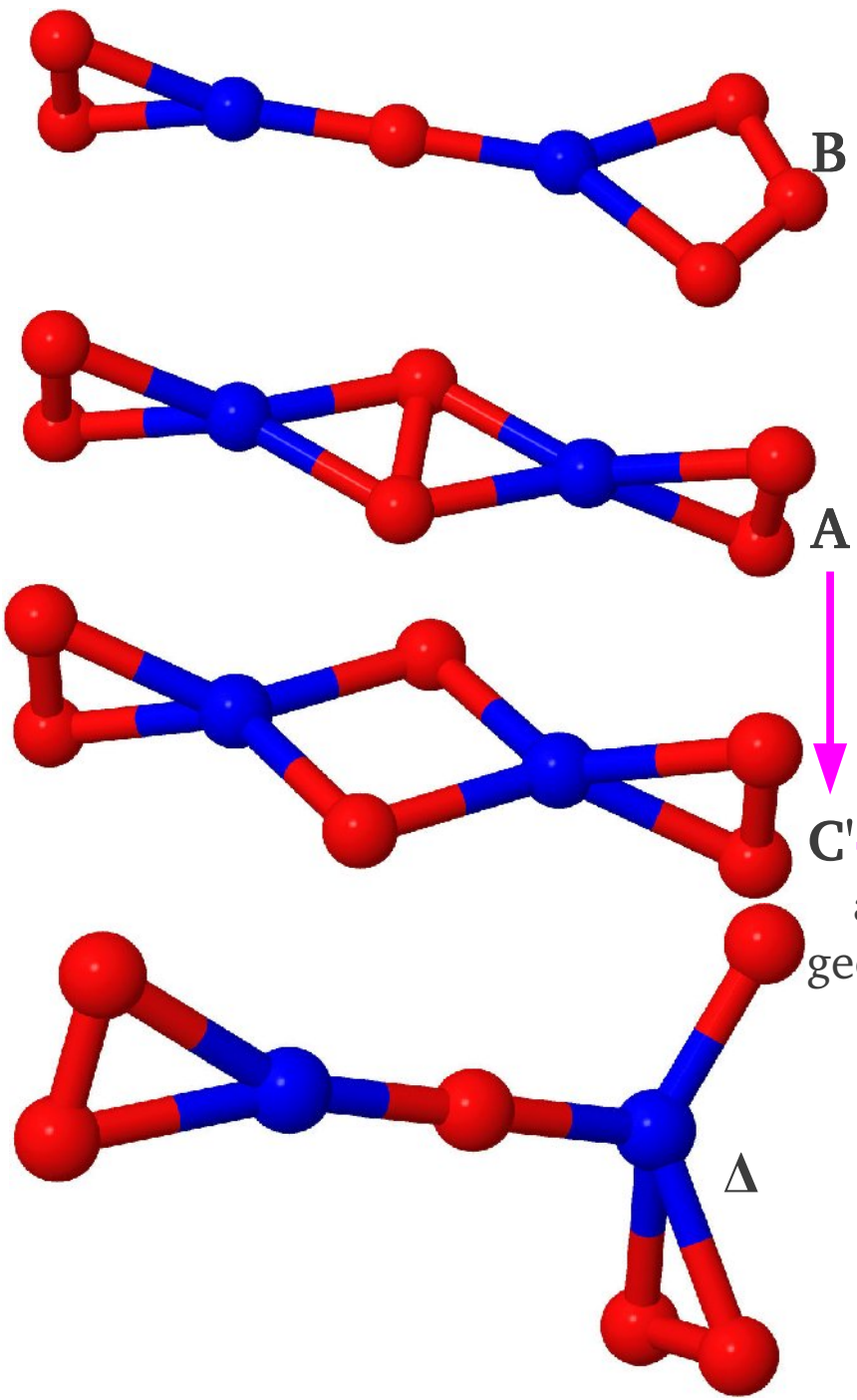


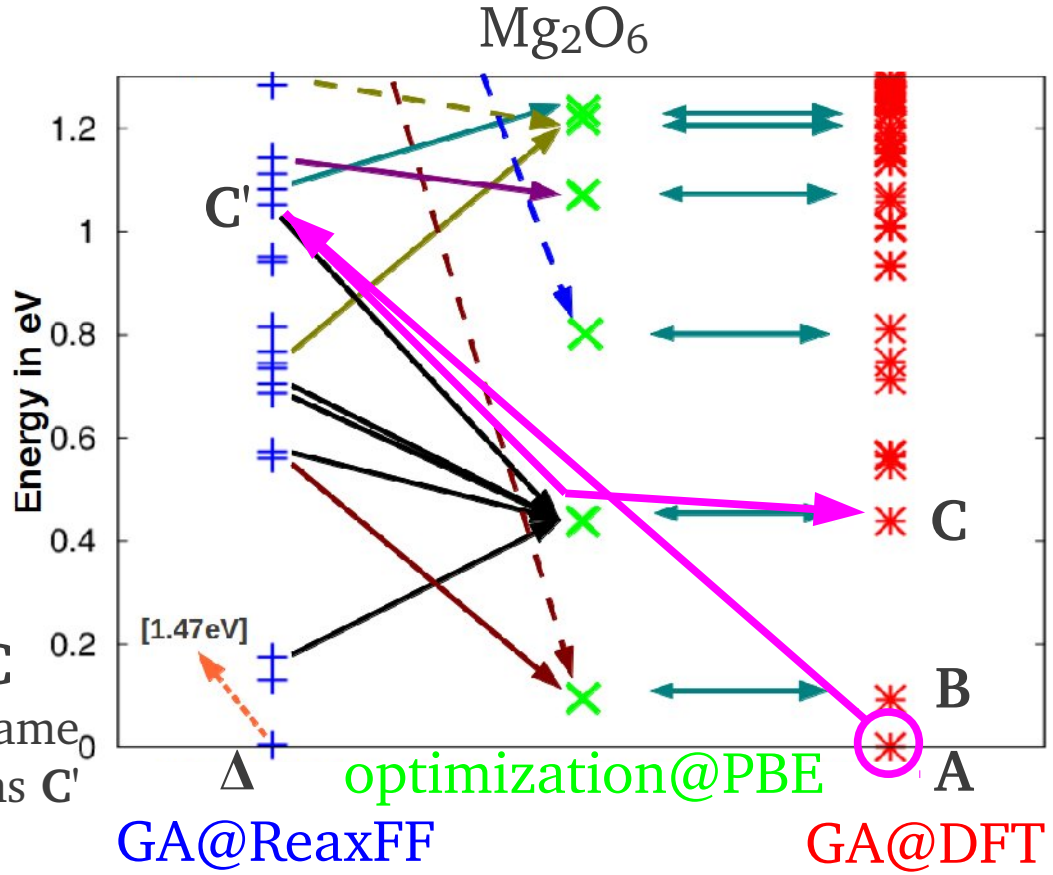


PBE after GA@reaxFF: OK

PBE after GA@reaxFF: GM missed

DFT as post-production applied to force field? NO !



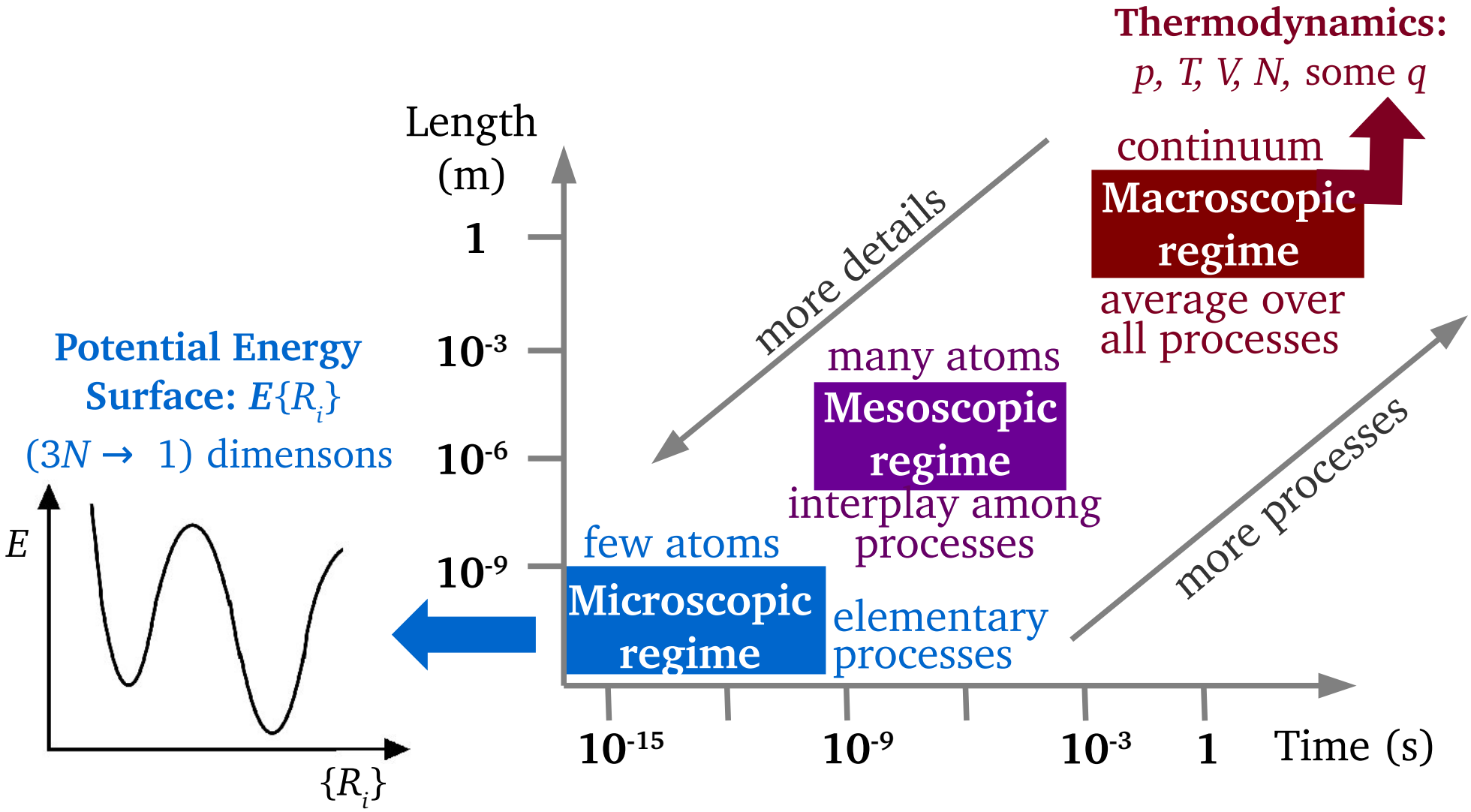


B is found by reaxFF, but not **A**
After optimization@reaxFF, **A** becomes **C'**
After optimization@PBE, **C'** becomes **C** ≠ **A**

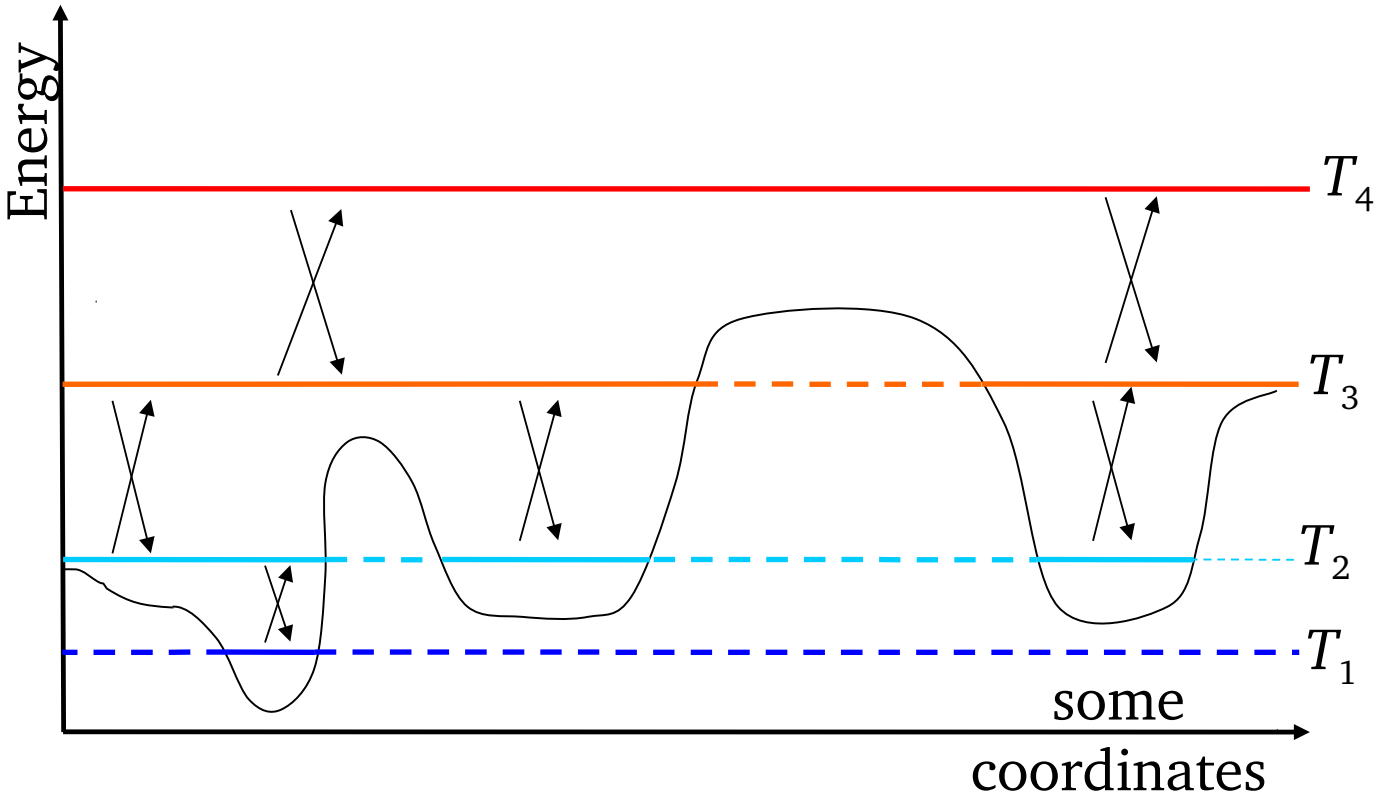
System in a fluxional
or liquid state:

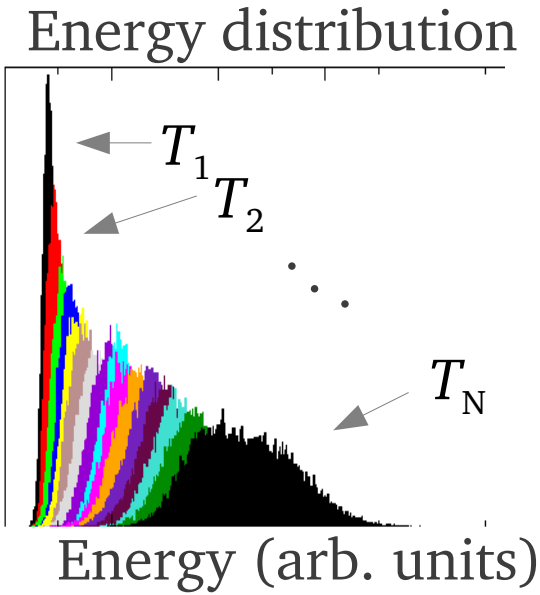
Ab initio
replica-exchange
molecular dynamics

Extending the scale



Replica exchange: the concept

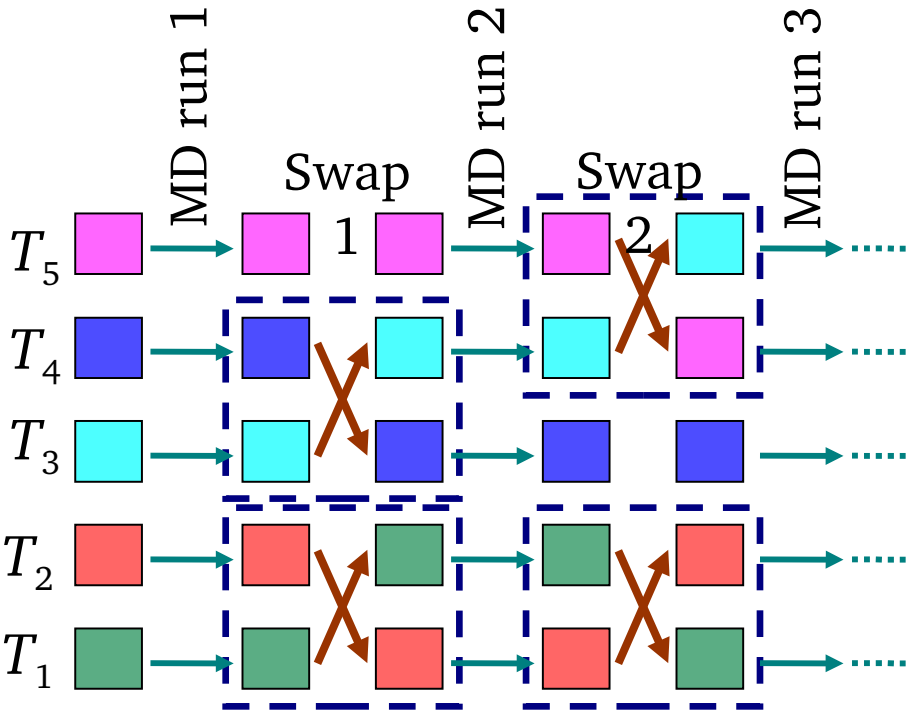


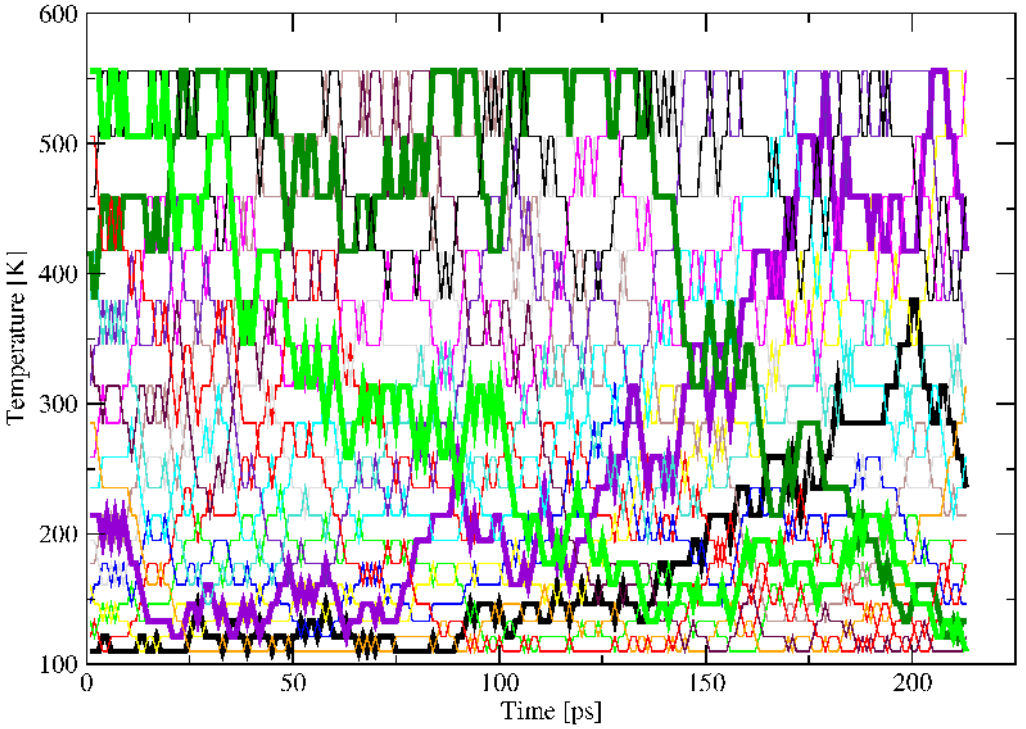


Exchange rule, ensuring canonical sampling at all temperatures:

$$P_{exchange} = \min\left(1, \exp(-(\beta_i - \beta_j)(U_i - U_j))\right)$$

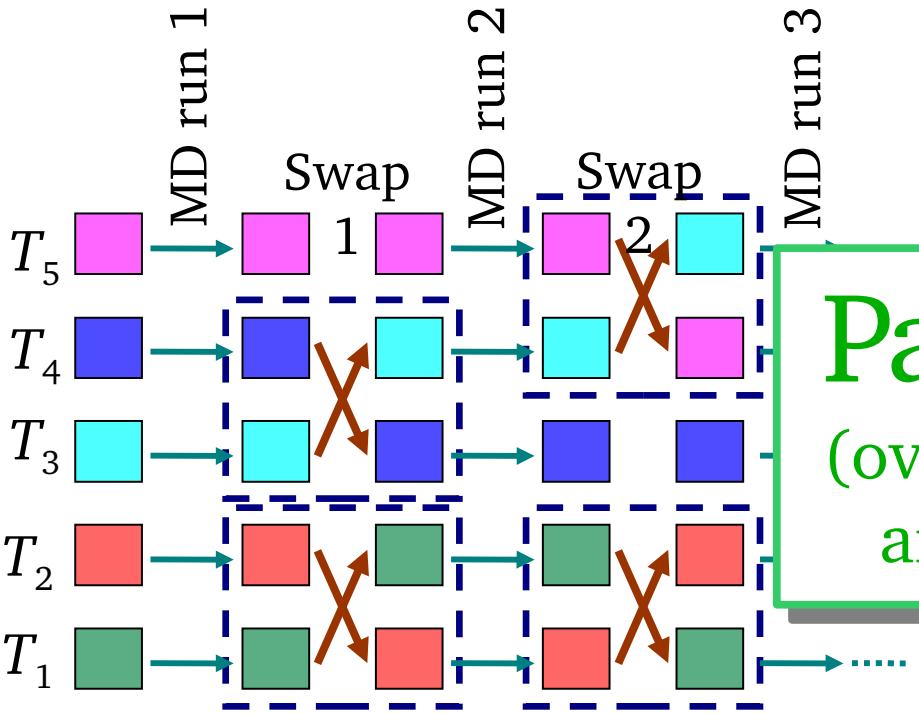
Replica exchange: the implementation



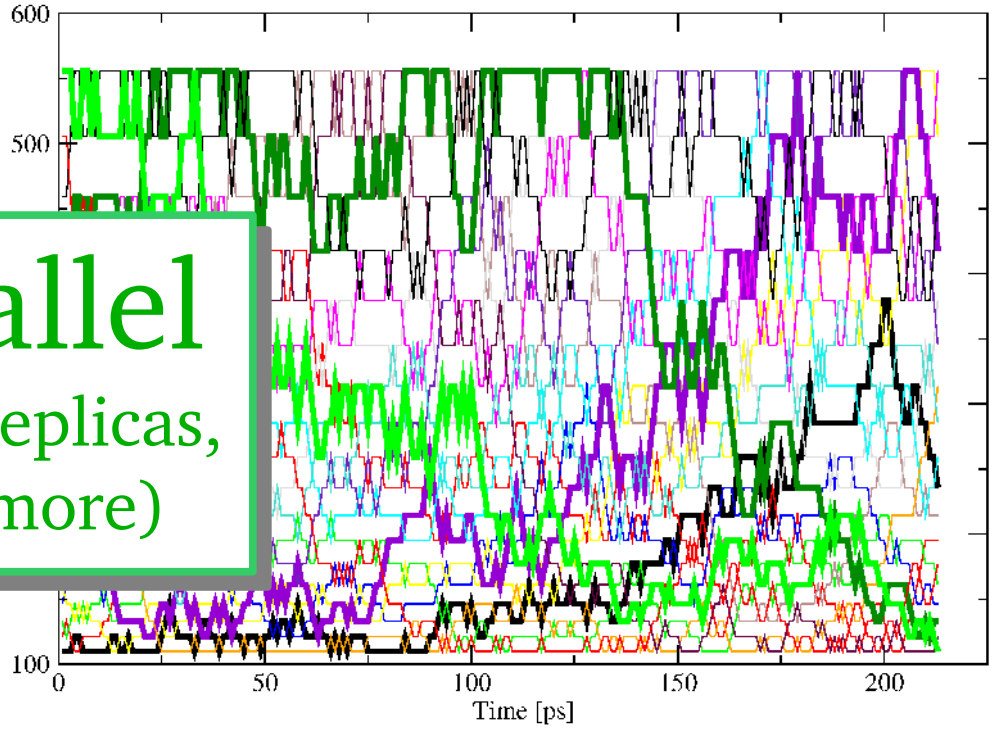


To be tuned for efficient sampling:
number of temperatures, list of temperatures, attempted swap frequency

Replica exchange: the implementation

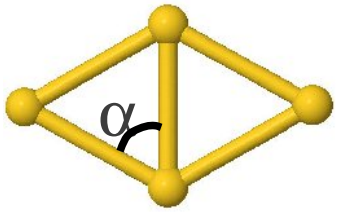


Parallel
(over replicas, and more)

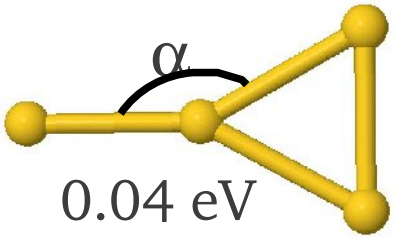


To be tuned for efficient sampling:
number of temperatures, list of temperatures, attempted swap frequency

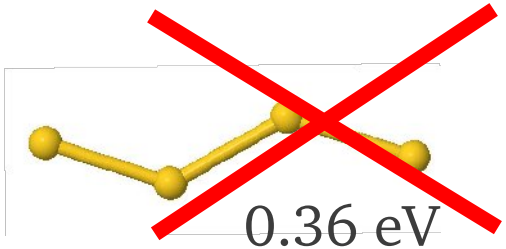
Au_4: coexistence of several isomers



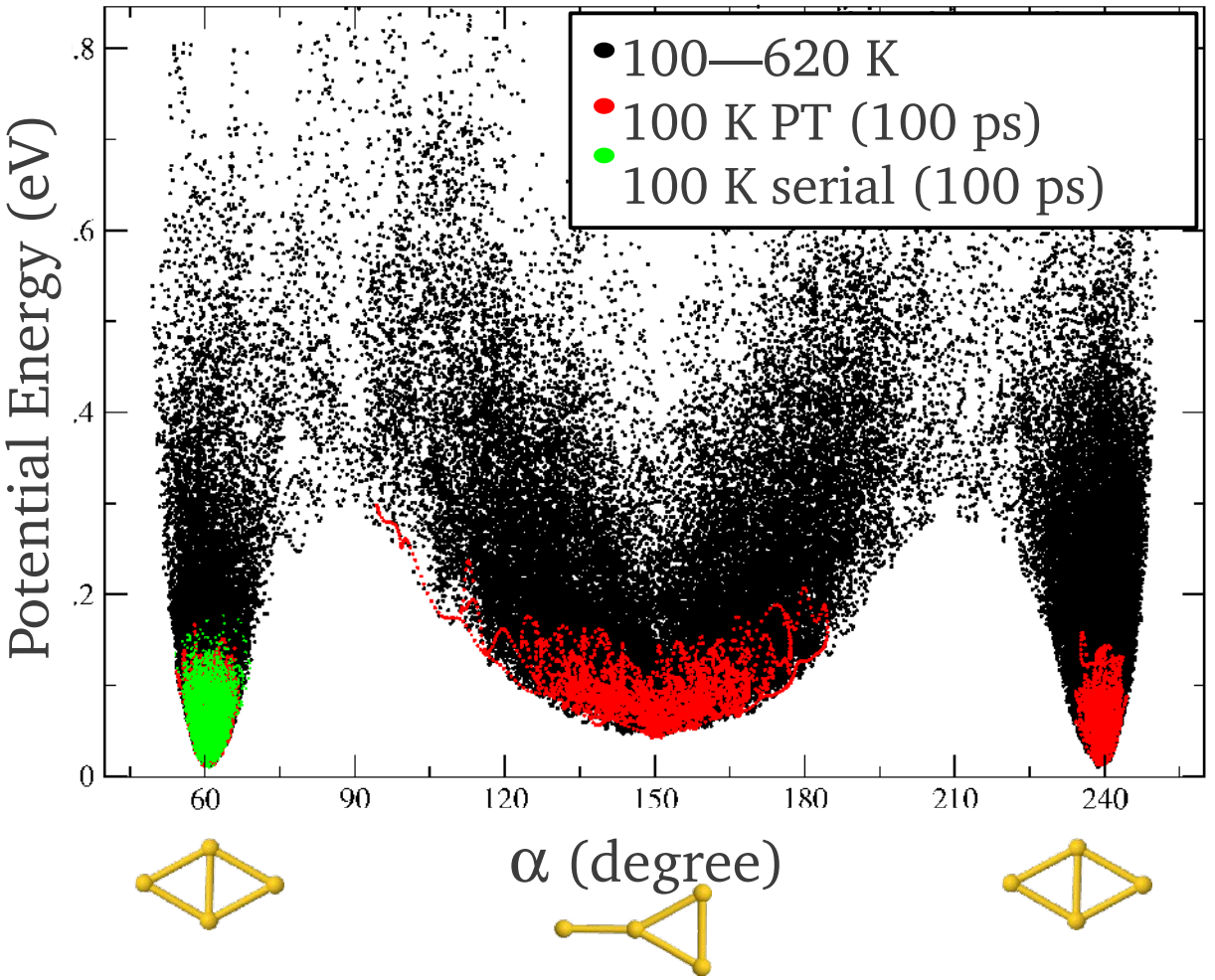
0.00 eV



0.04 eV



0.36 eV



Replica exchange: free energy?

Temperature-weighted Histogram Analysis Method:

Sampled probability

Re-weighting coefficients

$$P_i(q) = \mathrm{e}^{\beta_i F_i} c_i(q) P_0(q)$$

Un-biased probability at temperature β_0

normalization

q is chosen *a posteriori*

$$c_i(q) = \mathrm{e}^{-(\beta_i - \beta_0)U(q)} \mathrm{e}^{-\beta_i V_i(q)}$$, in case $H_i = H_0 + V_i(q)$

Iterative, self consistent solution of:

$$P_0(q) = \frac{\sum_{i=1}^{S} n_i(q)}{\sum_{i=1}^{S} N_i \mathrm{e}^{\beta_i F_i} c_i(q)}$$

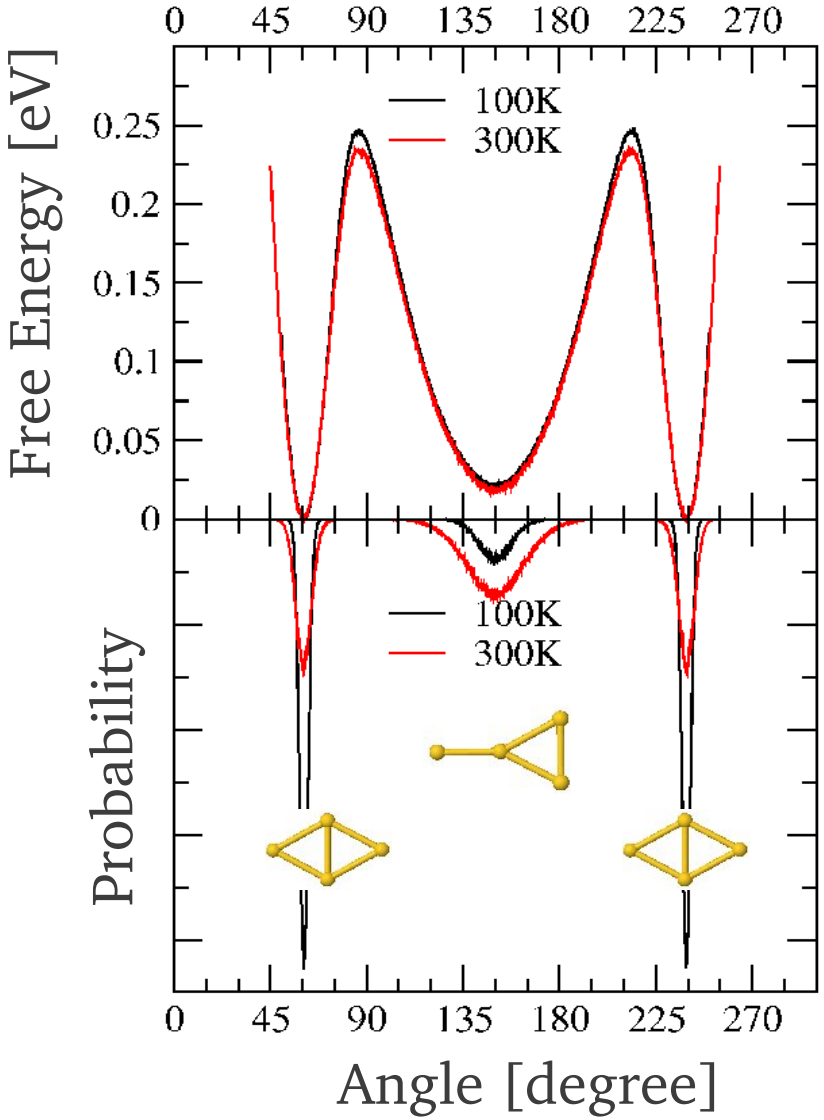
# of observations of q in bin i

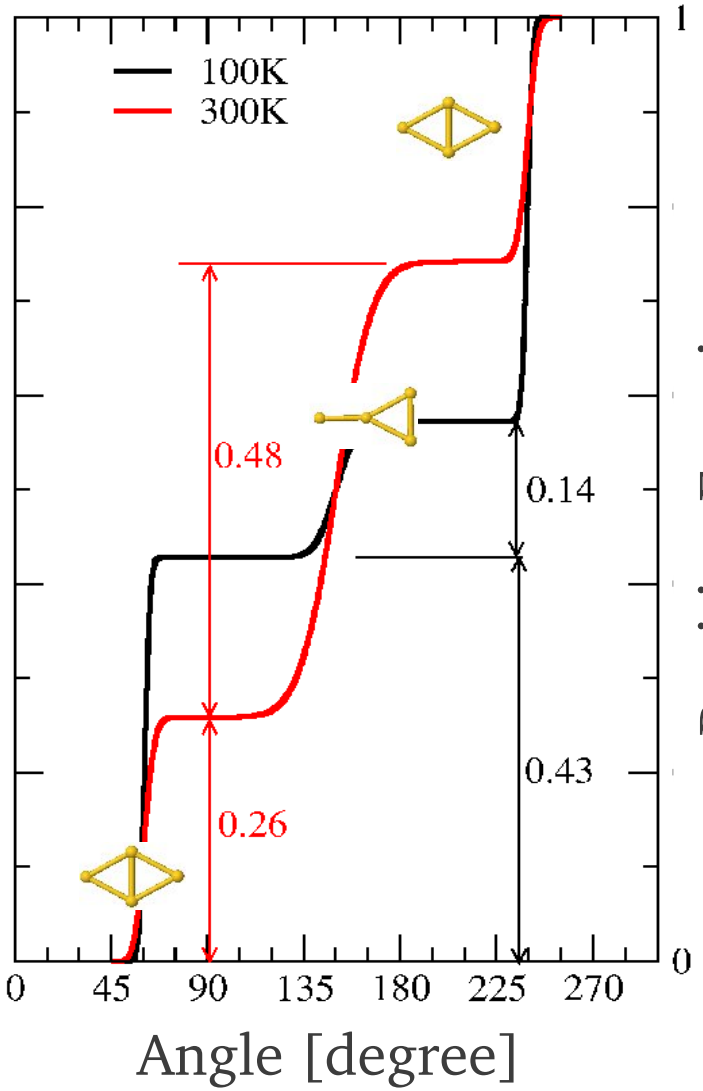
# of total observations in bin i

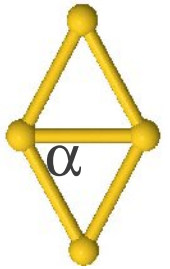
$$\beta_i F_i = -\ln\left(\int \mathrm{d}q \; c_i(q) P_0(q)\right)$$

IMPORTANT: "q" is a "post-production" (collective) variable

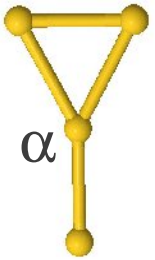
Au_4, relative population (T-WHAM)





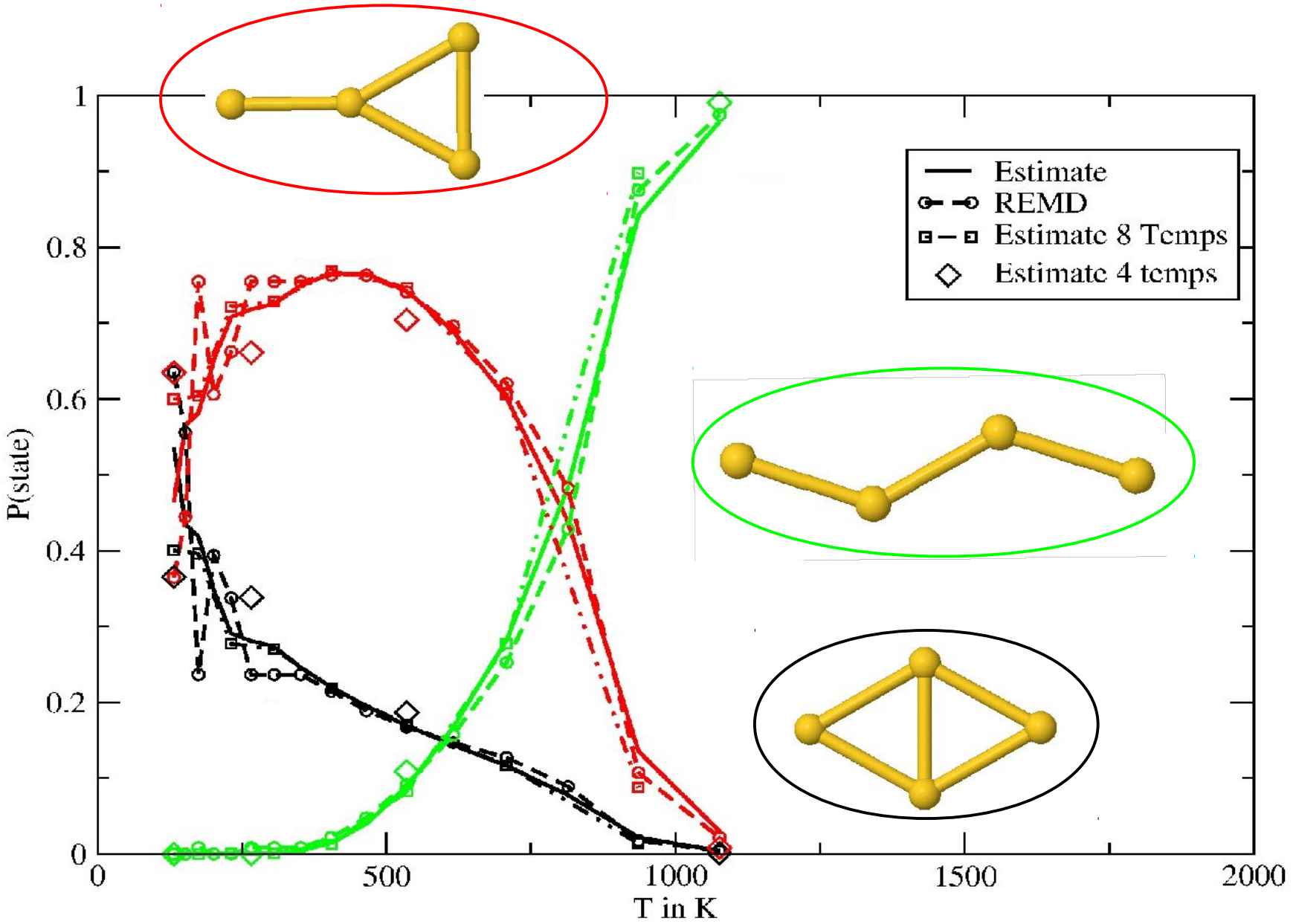


0.00 eV



0.04 eV
(PBE+vdW)

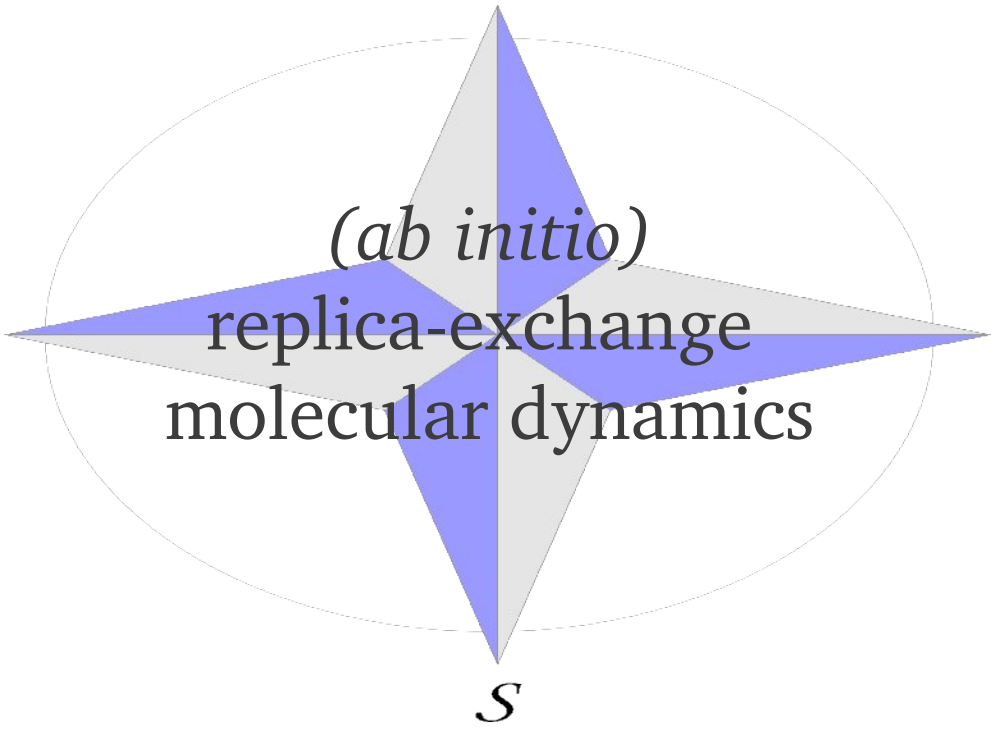
Au_4, relative population, coordination based descriptor



seamlessly multiscale:
bridges vibrational timescale
with state-hopping timescale

$\mathcal{N}$

unbiased search
for local minima $\mathcal{W}$



$\mathcal{E}$ *a posteriori*
evaluation of
free-energy
(can be refined)

$\mathcal{S}$

validation / tuning
of possibly biased
local-minima search algorithms
(e.g., genetic algorithm)

Conclusions

Temperature and other environmental (macroscopic) parameters affects the microscopic structure of a functional material

If the system is safely described as a collection of local minima:
a list of local minima is only a (necessary) starting point for understanding the thermodynamic stability
→ *ab initio* atomistic thermodynamics using *ab initio* data
Beware of anharmonic effects!

If the system is fluxional or liquid:
→ *ab initio* replica-exchange molecular dynamics (REMD)
(Configurational) entropy may be important not only in the "soft" colloidal and bio-molecular world, but also in the "hard" atomic (nano)world
Challenge: grand-canonical molecular dynamics scheme

The accurate (*ab initio*, but is also important which level of *ab initio*) description of the PES is necessary: temperature and time-average do not necessarily smear out the inaccuracies! Nonetheless, (good) force field are valuable (time-saving) starting points for an *ab initio* structural scanning.