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

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MAX-PLANCK-GESELLSCHAFT

We want to evaluate free energies and kinetics
We need accurate sampling of the potential-energy surface:
- (Free) energy of all relevant structures and
- (Free-) energy barriers of all relevant paths linking them

System as collection of
well-separated minima:
[(meta)stable states]

System in a fluxional
or liquid state:

Ab initio
atomistic thermodynamics

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:
[(meta)stable states]

Ab initio
atomistic thermodynamics

Ab initio atomistic thermodynamics

Consider several structures
Need to find "all of them"!

$\Longrightarrow$

Which ones are preferred
as a function of (T, p, μ, E_F)?

(DFT-)PES information

Average over time

Free energy

Microscopic

Macroscopic
(ensemble average)
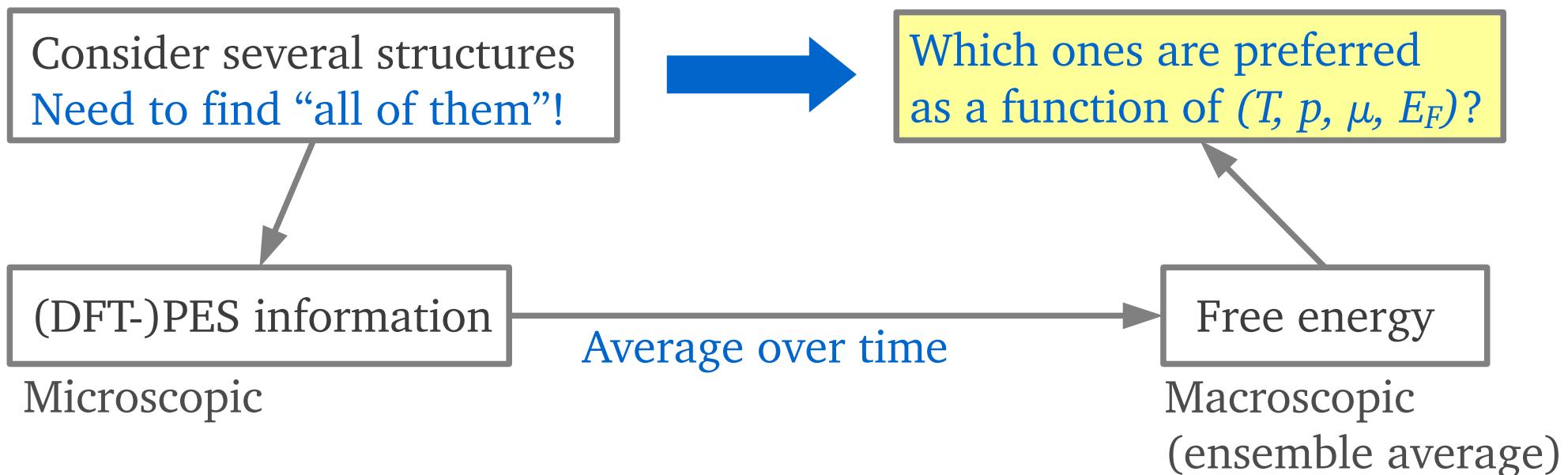
A surface is coupled to the gas (or liquid) above it
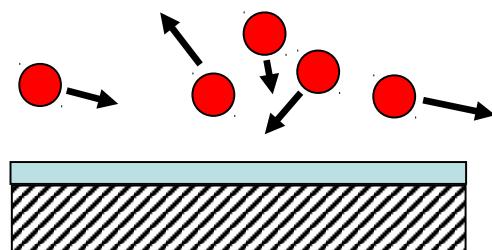
$$v = \frac{p}{\sqrt{2\pi\, mkT}}$$

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

$\Longrightarrow$

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

*K. Reuter, C. Stampfl, and M.Scheffler., in: Handbook of Materials Modeling, Vol. 1.
(Ed. Sid Yip), Springer 2005.*

Ab initio atomistic thermodynamics

Showcase: Mg clusters in oxygen (-containing) atmosphere

Formation free energy   Free energy of pristine surface/cluster

$$\Delta G_{\mathrm{f}}(T, p_{\mathrm{O}_2}) = F_{\mathrm{Mg}_M\mathrm{O}_x}(T) - F_{\mathrm{Mg}_M}(T) - x\mu_O(T, p_{\mathrm{O}_2})$$

Free energy of surface/cluster + ligand(s)   Chemical potential of ligand(s)

zero-point energy

$$F(T) = E^{\mathrm{DFT}} + E^{\mathrm{ZP}} +$$
$$- T\left[S^{\mathrm{tr}}(T) + S^{\mathrm{rot}}(T) + S^{\mathrm{symm}}(T) + S^{\mathrm{spin}}(T) + S^{\mathrm{vib}}(T)\right]$$

translational   rotational   vibrational

K. Reuter, C. Stampfl, and M.Scheffler., in: Handbook of Materials Modeling, Vol. 1. (Ed. Sid Yip), Springer 2005.

Initialization: force field

Selection initial *pool*
Diversity!

↓

Local optimization
with FF (reaxFF [1])

↓

Evaluation of
energy and *fitness*

↓

New structure?
update *pool*

↓

Selection of *parents*,
crossover, *mutation*

Fitness: mapping
[Energy MAX, Energy min] → [0, 1]
If fitness ~ 1 then high chance to be
selected for mating

Genetic algorithm jargon:
- two (or more...) structures are
selected as *parents* on the basis of
high fitness.
- they are combined through a
crossover process
- some features of the newly
formed structure are *mutated*

[1] A. van Duin *et al.*, J. Chem. Phys. A **105**, 9396 (2001)

Which structures? **Unbiased** search: *cascade* genetic algorithm

Initialization: force field

- Selection initial *pool* Diversity!
- Local optimization with FF (reaxFF [1])
- Evaluation of energy and *fitness*
- New structure? update *pool*
- Selection of *parents, crossover, mutation*

Actual scanning: DFT in cascade

- Initial pool from FFGA
- Local optimization with "light DFT" (PBE+vdW)
- Early rejection of known structures
- Local optimization with "tight DFT" (PBE+vdW)
- Evaluation of *fitness*: Energy with High-level DFT (PBE0+vdW)
- New structure? update pool
- Selection *parents, crossover, mutation*

Which structures? **Unbiased** search: *cascade* genetic algorithm

Initialization: force field

Selection initial *pool*

It works only if light settings give already reasonable structures
- E.g., well selected local-orbital basis set (FHI-aims, SIESTA): **OK**
- E.g., plane waves: **NOT OK**

Evaluation of energy and *fitness*

New structure? update *pool*

Selection of *parents*, *crossover*, *mutation*

Actual scanning: DFT in cascade

Initial pool from FFGA

Local optimization with "light DFT" (PBE+vdW)

Early rejection of known structures

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Selection *parents*, *crossover*, *mutation*

New structure? update pool

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Which structures? **Unbiased** search: *cascade* genetic algorithm

Initialization: force field

Actual scanning: DFT in cascade
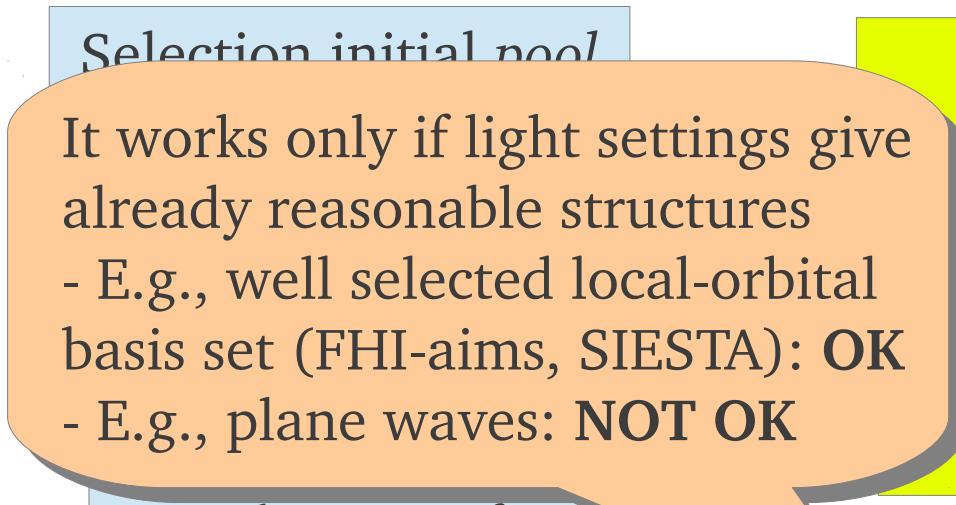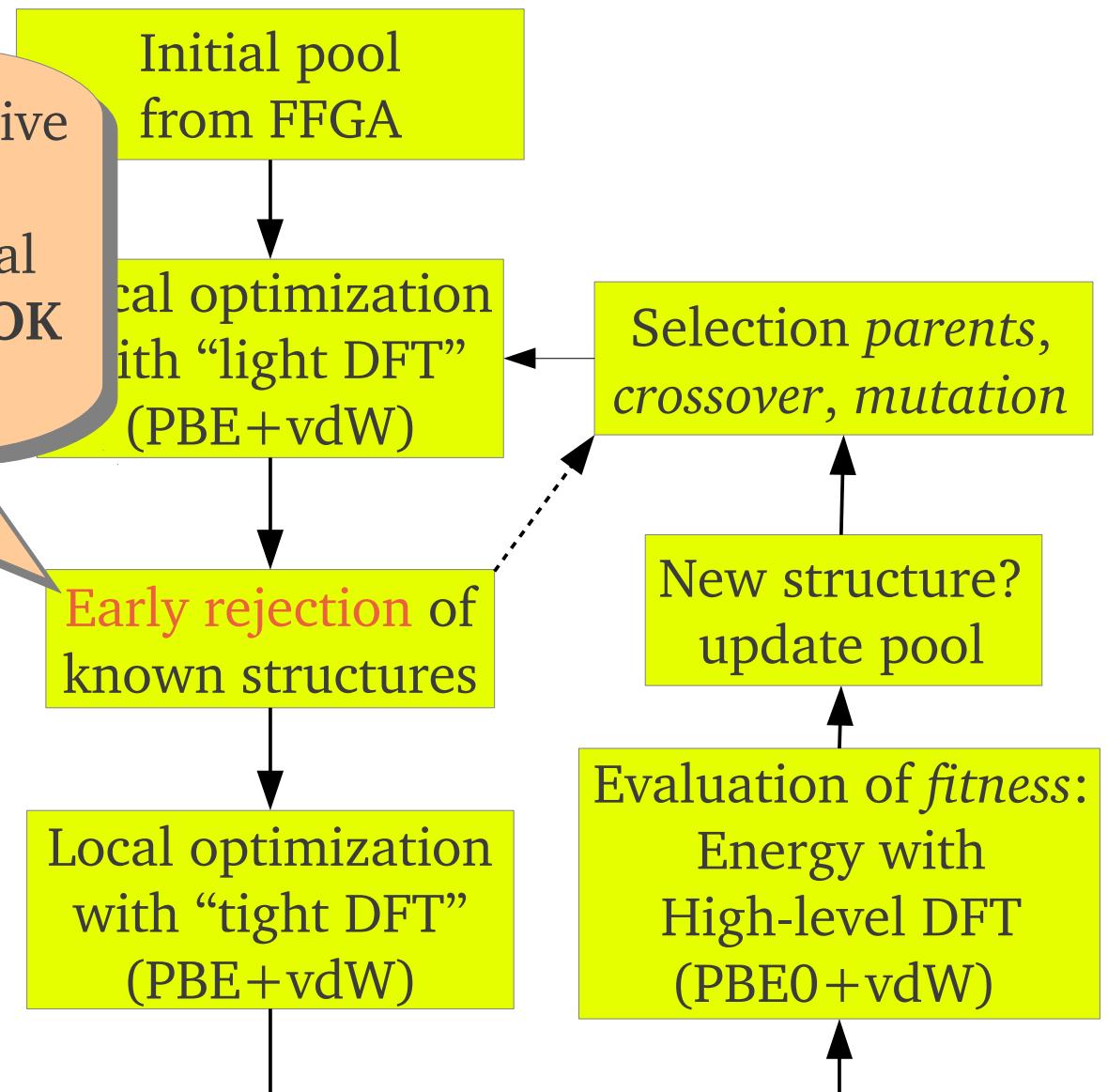
Selection initial *pool*
Diversity!

Local optimization
with FF (reaxh...

Evaluation...
energy and *fi...*

New structu...
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Selection of *parents,*
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Initial pool
from FFGA

Local optimization

...tion *parents,*
...ver, mutation

...y structure?
...date pool

Local optimization
with "tight DFT"
(PBE+vdW)

...ation of *fitness:*
Energy with
High-level DFT
(PBE0+vdW)

Validation of this scheme possible?

Yes,
with replica-exchange
molecular dynamics

Why a reactive force field?

Example of a non-reactive force field (e.g., CHARMM [1]):

$$V = E_{\text{bonds}} + E_{\text{angles}} + E_{\text{torsions}} + E_{\text{out-of-plane}} + E_{\text{non-bonded}} + E_{\text{coulomb}} =$$

$$= \sum_{\text{bonds}} k_b(b - b_0)^2 + \sum_{\text{angles}} k_\theta(\theta - \theta_0)^2 + \ldots$$

No chemistry: bond connectivity is fixed once and forever

[1] BR Brooks, RE Bruccoleri, BD Olafson, DJ States, S Swaminathan, **M Karplus**, J Comp Chem 4 187 (1983)

Example of a simple reactive potential: (Brenner) bond-order potential [2]:

Repulsive   Attractive

$$E_b = \frac{1}{2} \sum_i \sum_{j \neq i} \left[V^R(r_{ij}) - b_{ij} V^A(r_{ij}) \right]$$

Bond order

$$b_{ij} = \left[1 + \sum_{k \neq i,j} f_c(r_{ik}) G(\cos \theta_{kij}) \right]^{-1/2} \sim (1 + \#\text{neighbors})^{-1/2}$$

[2] DW Brenner, Phys. Rev. B 42, 9458 (1990)

Bond order, in figures

Repulsive   Attractive

$$E_b = \frac{1}{2} \sum_i \sum_{j \neq i} \left[\boxed{V^R(r_{ij})} - \boxed{b_{ij}} \boxed{V^A(r_{ij})} \right]$$

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A reactive FF for all elements, e.g., reaxFF [2]
(alternative, Empirical Valence Bond [3]):

$$E_{\text{system}} = E_{\text{bond}} + E_{\text{over}} + E_{\text{under}} + E_{\text{val}} + E_{\text{pen}} + E_{\text{tors}} +$$

$$E_{\text{conj}} + E_{\text{vdWaals}} + E_{\text{Coulomb}}$$

E_{bond} depends on "bond order", which depends on environment
(e.g., number of first neighbours to both atoms forming a bond)

[2] A. van Duin *et al.*, J. Chem. Phys. A **105**, 9396 (2001)
[3] S.C.L. Kamerlin and **A. Warshel**, Wiley Interdisciplinary Reviews: Computational Molecular Science 1, 30 (2011)

Why a reactive force field?

Example of a non-reactive force field (e.g., CHARMM [1]):

$$V = \boxed{\text{Energies are meaningfully associated only to a subset of the configurational space}}$$

$$= \sum_{\text{bonds}} k_b (b - b_0)^2 + \sum_{\text{angles}} k_\theta (\theta - \theta_0)^2 + ...$$

No chemistry: bond connectivity is fixed once and forever

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$$E_{\text{system}} = E_{\text{bond}} + E_{\text{over}} + E_{\text{under}} + E_{\text{val}} + E_{\text{pen}} + E_{\text{tors}} +$$

In principle, a *meaningful* energy is associated
to any configuration of the atoms in the systems

[2] A. van Duin *et al.*, J. Chem. Phys. A **105**, 9396 (2001)

[3] S.C.L. Kamerlin and **A. Warshel**, Wiley Interdisciplinary Reviews: Computational Molecular Science 1, 30 (2011)

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

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Free energy? Harmonic, beyond, and further beyond

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

$$F^{\text{vib}}(T) = E^{\text{ZP}} - T S^{\text{vib}}(T) = \sum_{i=1}^{\#DoF} \frac{h\nu_i}{2} + k_{\text{B}} T \sum_{i=1}^{\#DoF} \ln\left(1 - \exp\left(\frac{h\nu_i}{k_{\text{B}} T}\right)\right)$$

Input: evaluation of harmonic spectrum

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

Total energy   Potential energy   Kinetic energy

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

DFT total energy of 0K structure

Harmonic F

Input: from NVT molecular dynamics

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

Free energy? Harmonic, beyond, and further beyond

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

$$F^{\text{vib}}(T) = E^{\text{ZP}} - TS^{\text{vib}}(T) = \sum_{i=1}^{\#DoF} \frac{h\nu_i}{2} + k_{\text{B}}T \sum_{i=1}^{\#DoF} \ln\left(1 - \exp\left(\frac{h\nu_i}{k_{\text{B}}T}\right)\right)$$

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

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

- Multiple minima: multi-canonical methods, replica exchange

Ab initio atomistic thermodynamics

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

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

$$F(T) = E^{\mathrm{DFT}} + E^{\mathrm{ZP}} + \\ - T\left[S^{\mathrm{tr}}(T) + S^{\mathrm{rot}}(T) + S^{\mathrm{symm}}(T) + S^{\mathrm{spin}}(T) + S^{\mathrm{vib}}(T)\right]$$

K. Reuter, C. Stampfl, and M.Scheffler., in: Handbook of Materials Modeling, Vol. 1.
(Ed. Sid Yip), Springer 2005.

Ab initio atomistic thermodynamics: phase diagrams
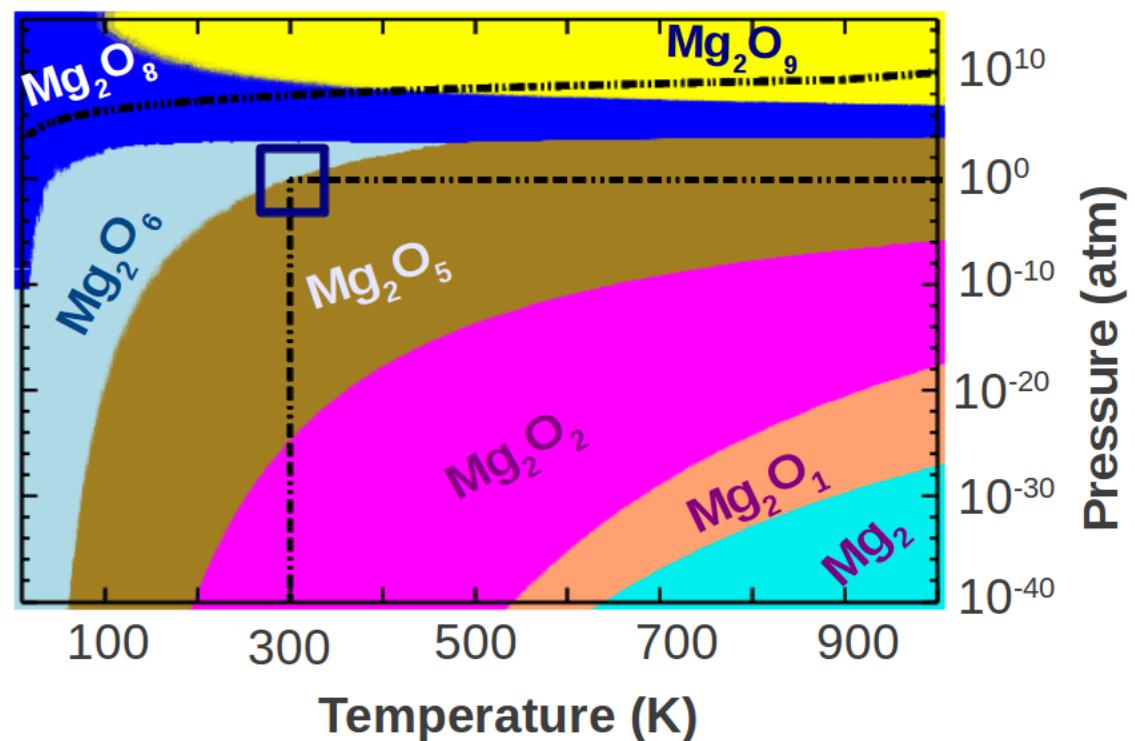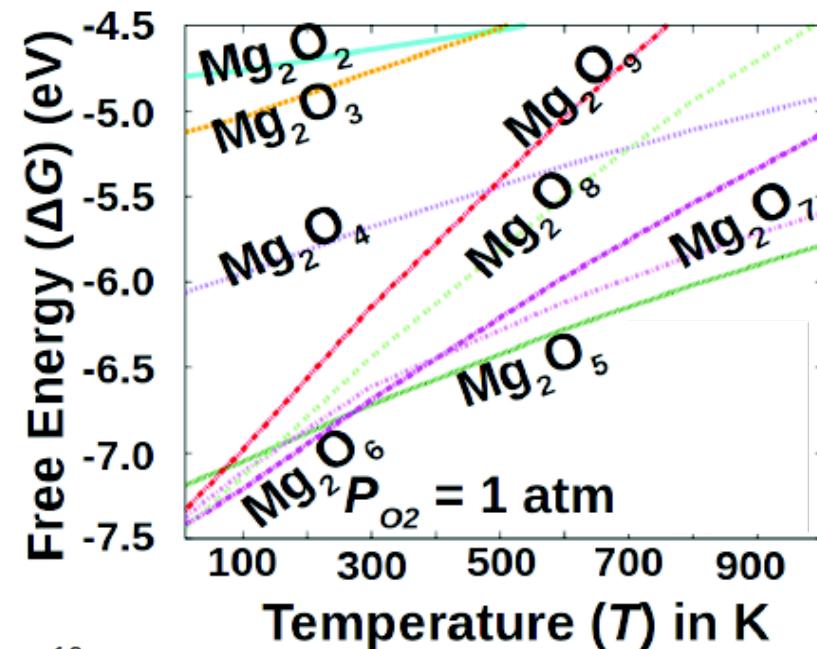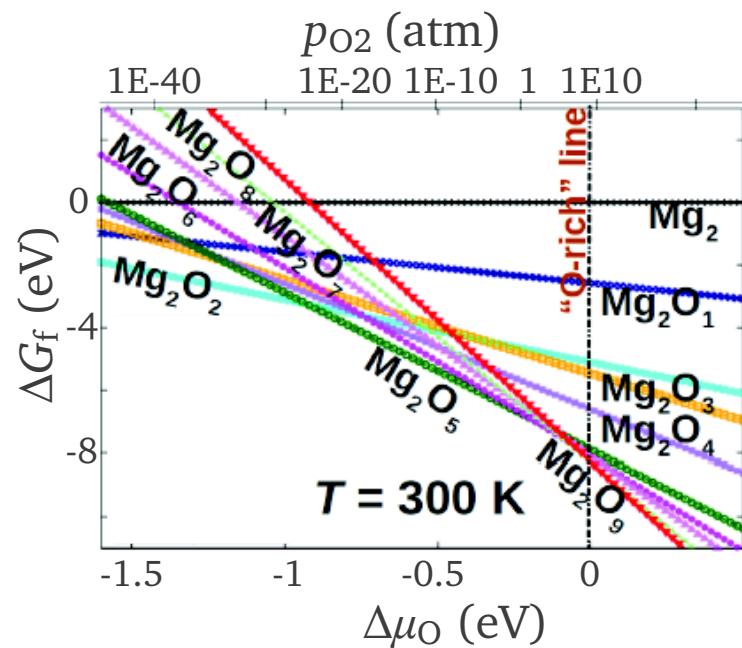
Validation of the total-energy method
(accuracy of the potential-energy surface)

Case study: reaxFF vs DFT for Mg_MO_x clusters

Benchmarking GGA and hybrid functionals

Legend:
- ✕–✕ reaxFF
- ● PBE+vdW
- ▲ PBE0+vdW
- ▼ rPT2@PBE

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)

Among the (reactive) force fields designed for a wide class of elements, reaxFF is possibly the best.
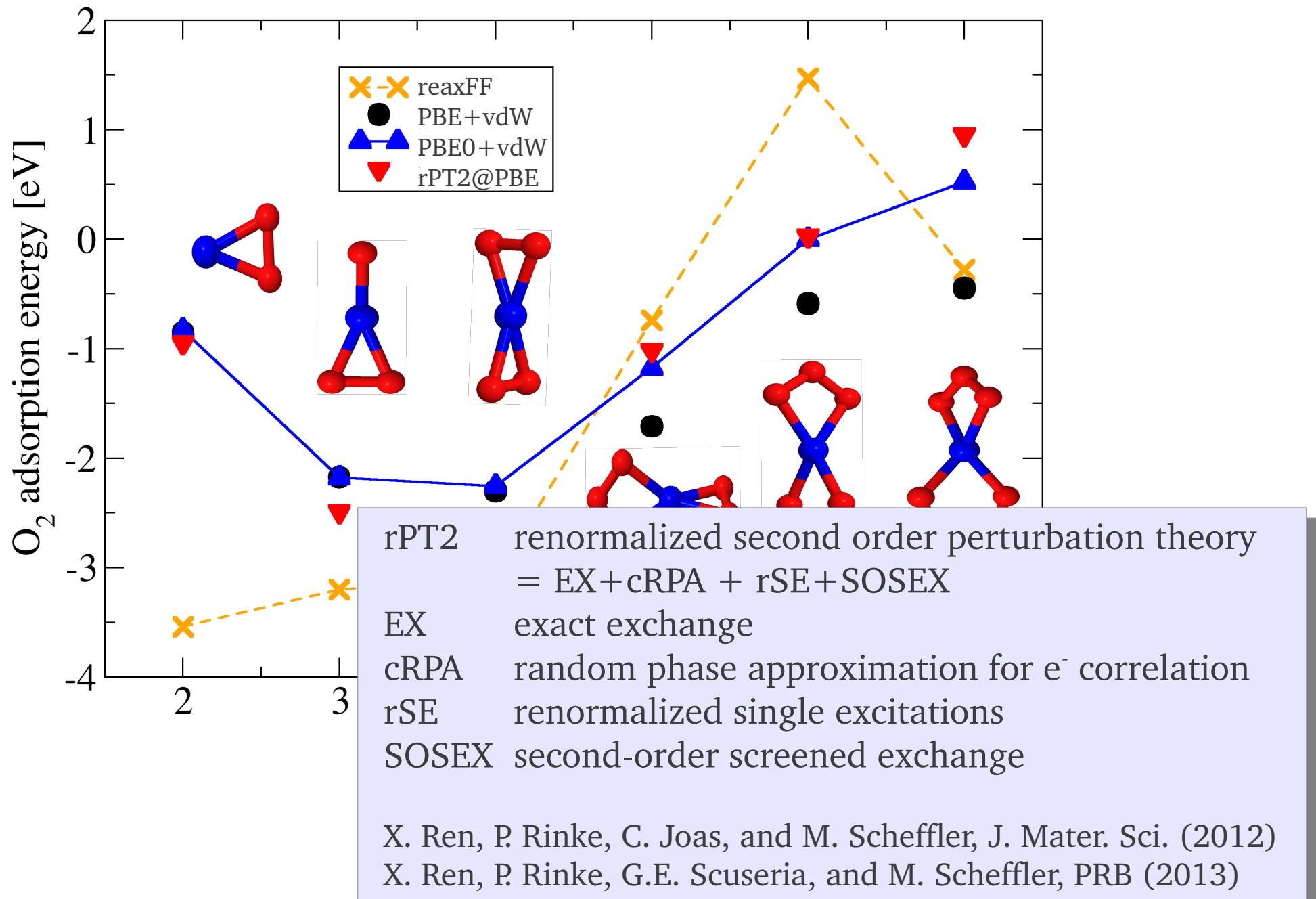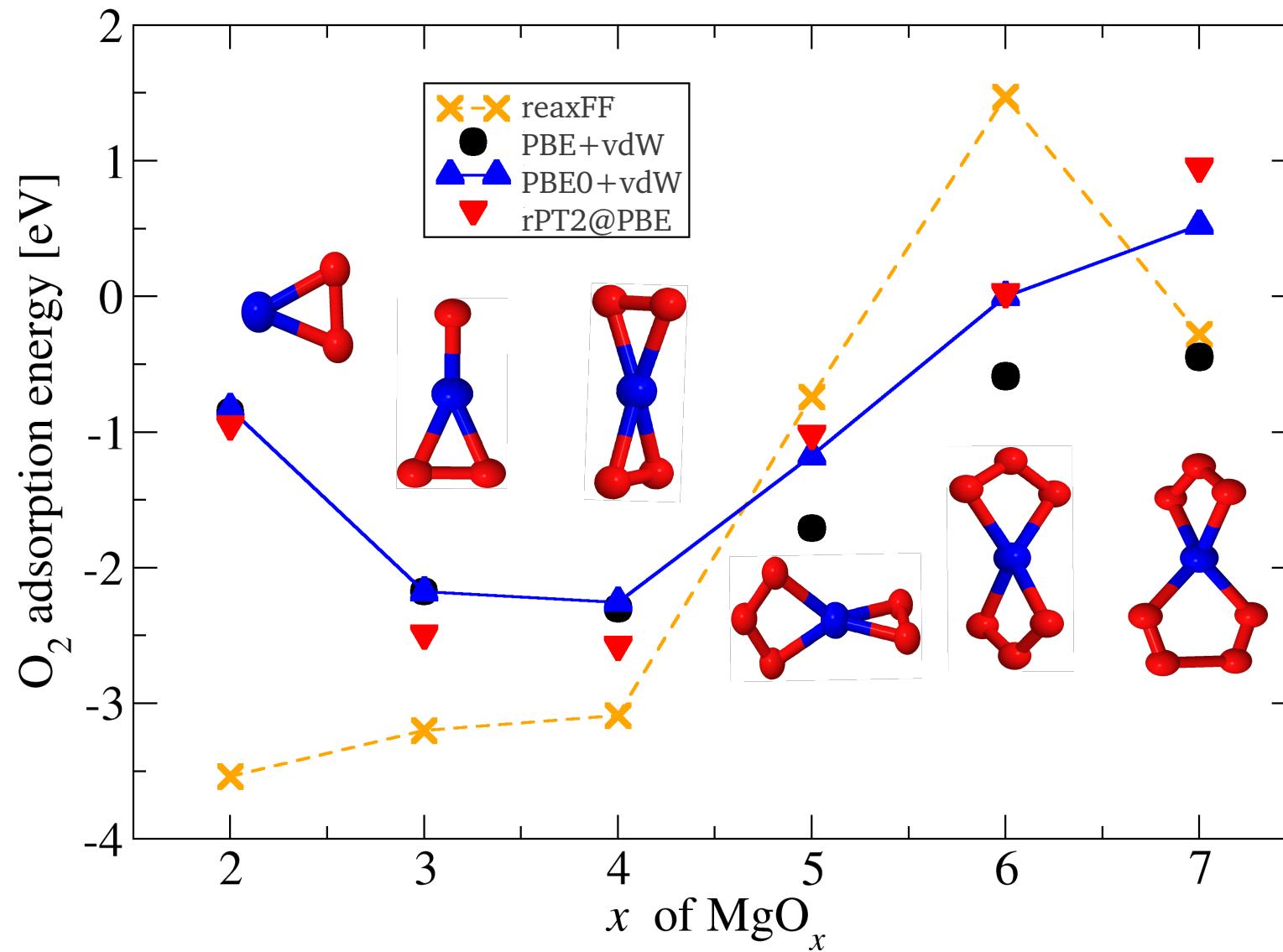
However the "range of validity" of the reaxFF is narrow and only covering those situations that were used to fit its parameters.

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

Mg₂Oₓ phase diagram: ReaxFF vs PBE+vdW "light" and "tight"

Condensation of oxygen droplets
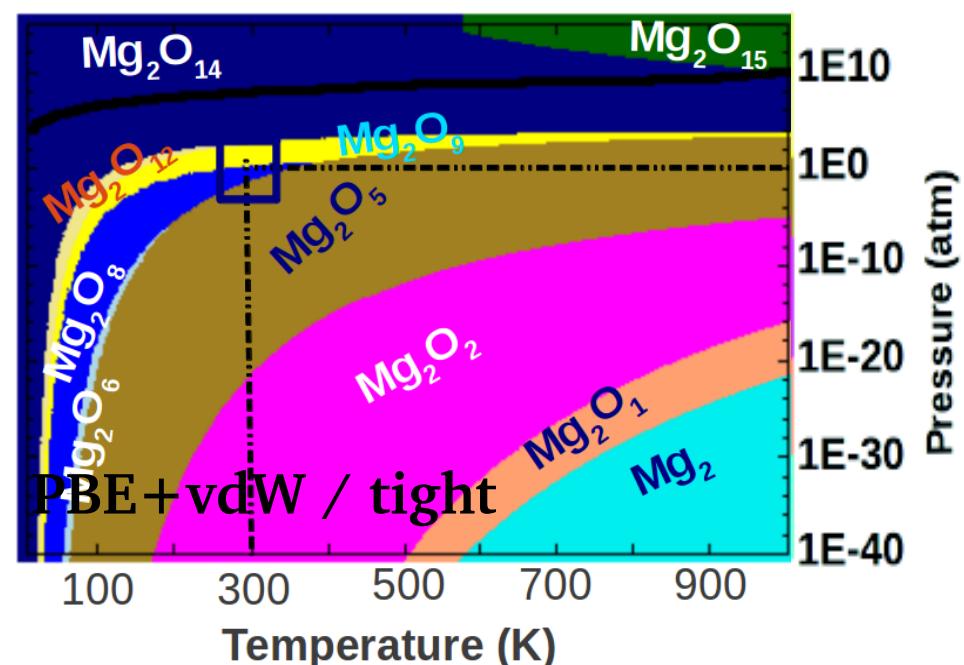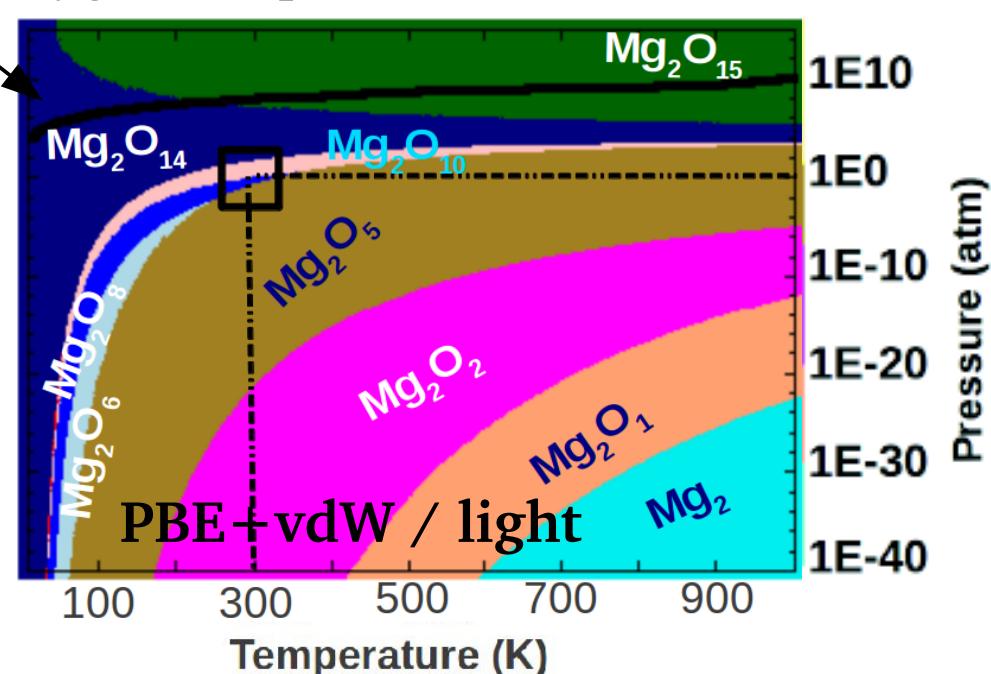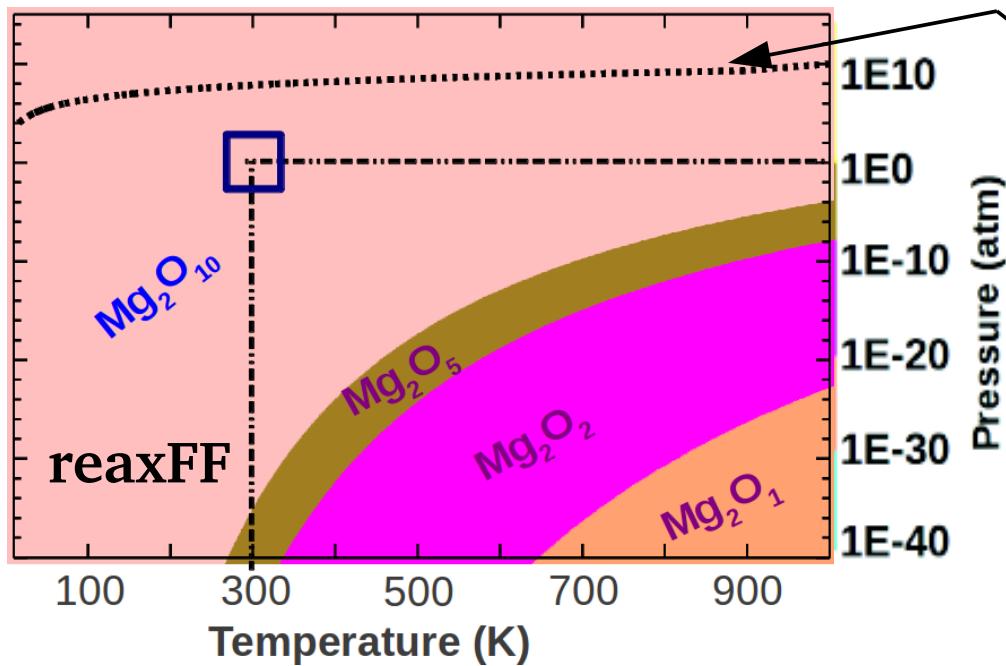
Condensation of oxygen droplets

Mg$_2$O$_x$ phase diagram: ReaxFF vs PBE+vdW vs PBE0+vdW vs rPT2

Condensation of oxygen droplets

Mg$_2$O$_x$ phase diagram: ReaxFF vs PBE+vdW vs PBE0+vdW vs rPT2

Condensation of oxygen droplets

- ReaxFF *and* PBE(+vdW) phase diagrams fail badly in the most interesting region
- PBE0(+vdW) are accurate wrt the reference (rPT2@PBE) at all relevant conditions
- not to be forgotten that a full-PBE0(+vdW) scan of the PES wold be prohibitive
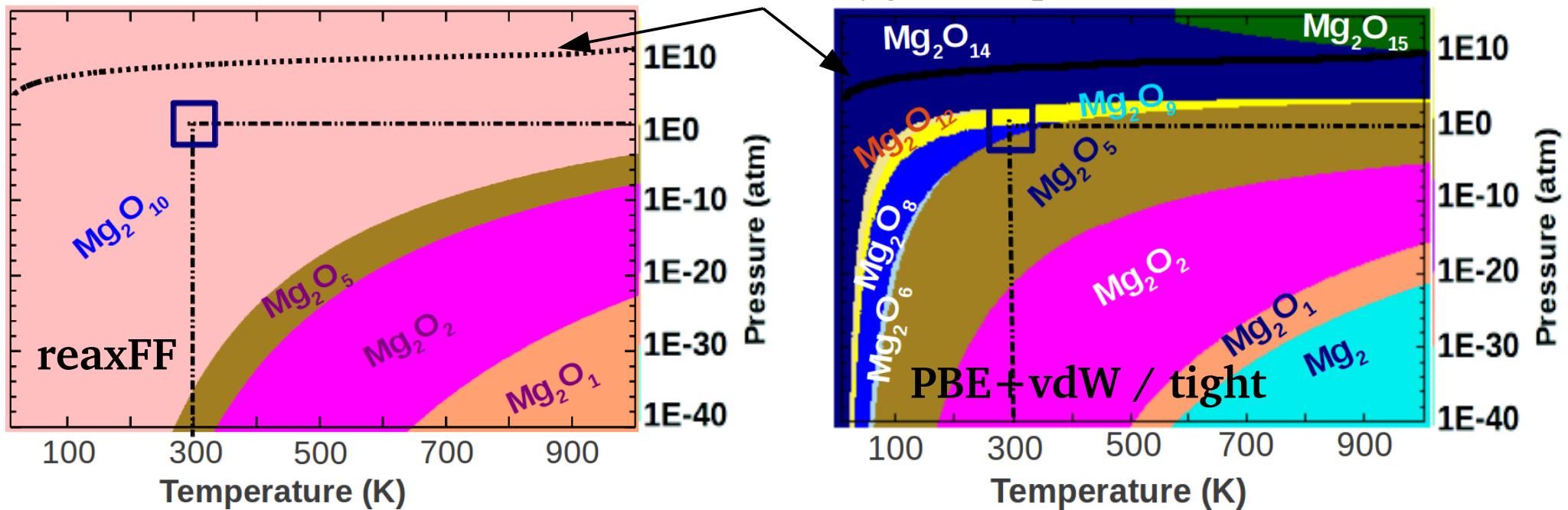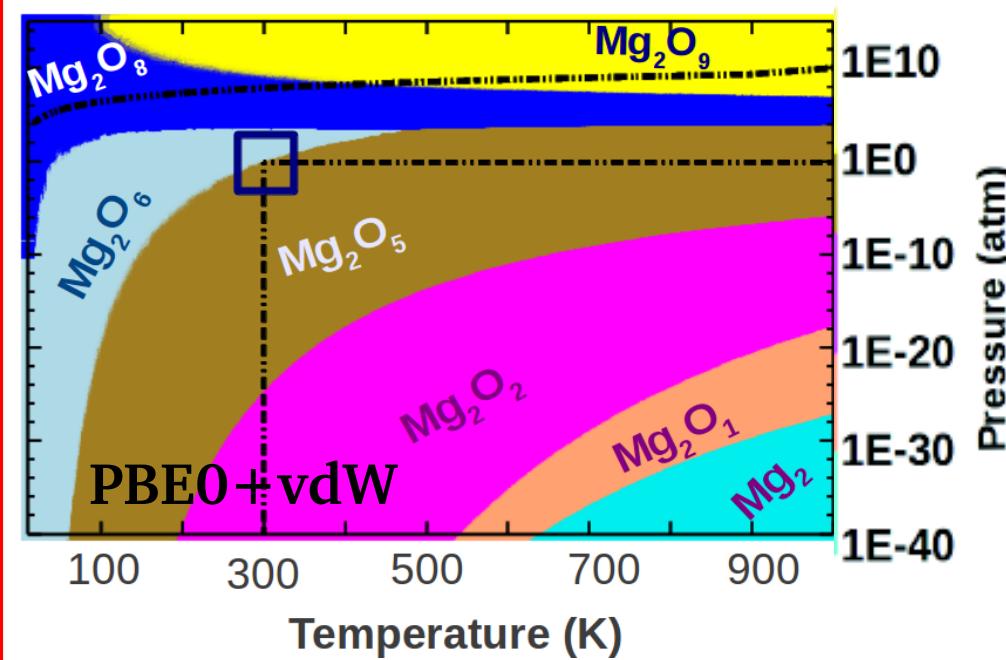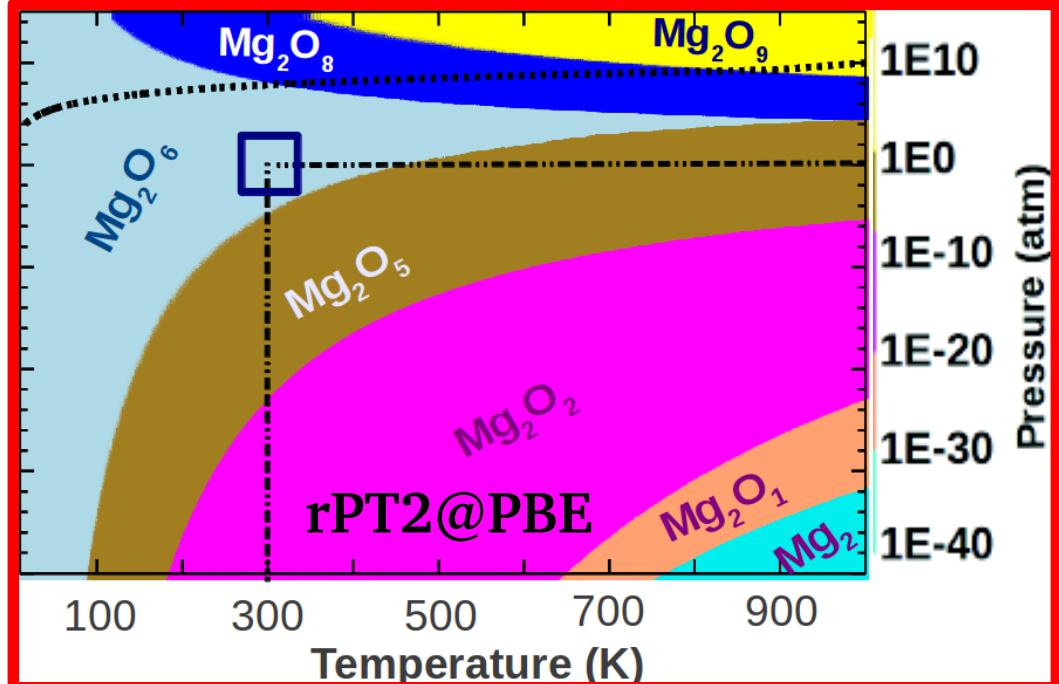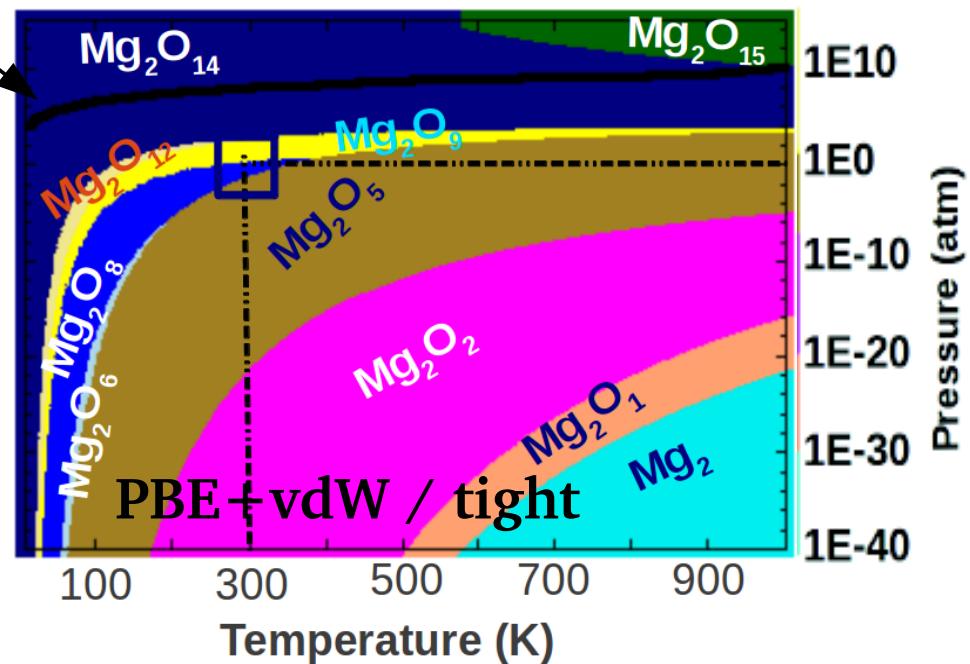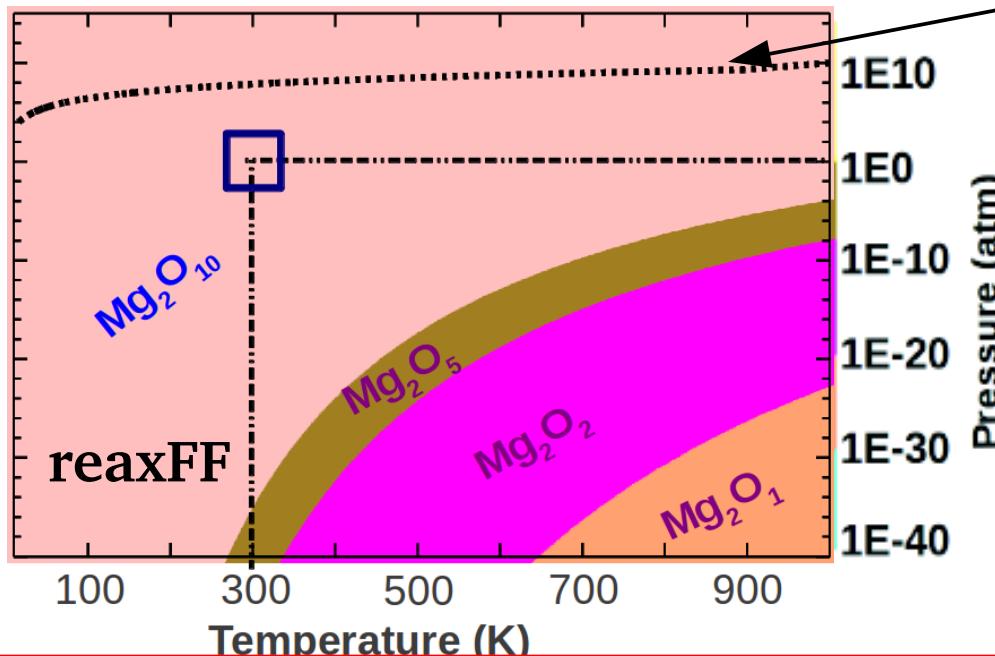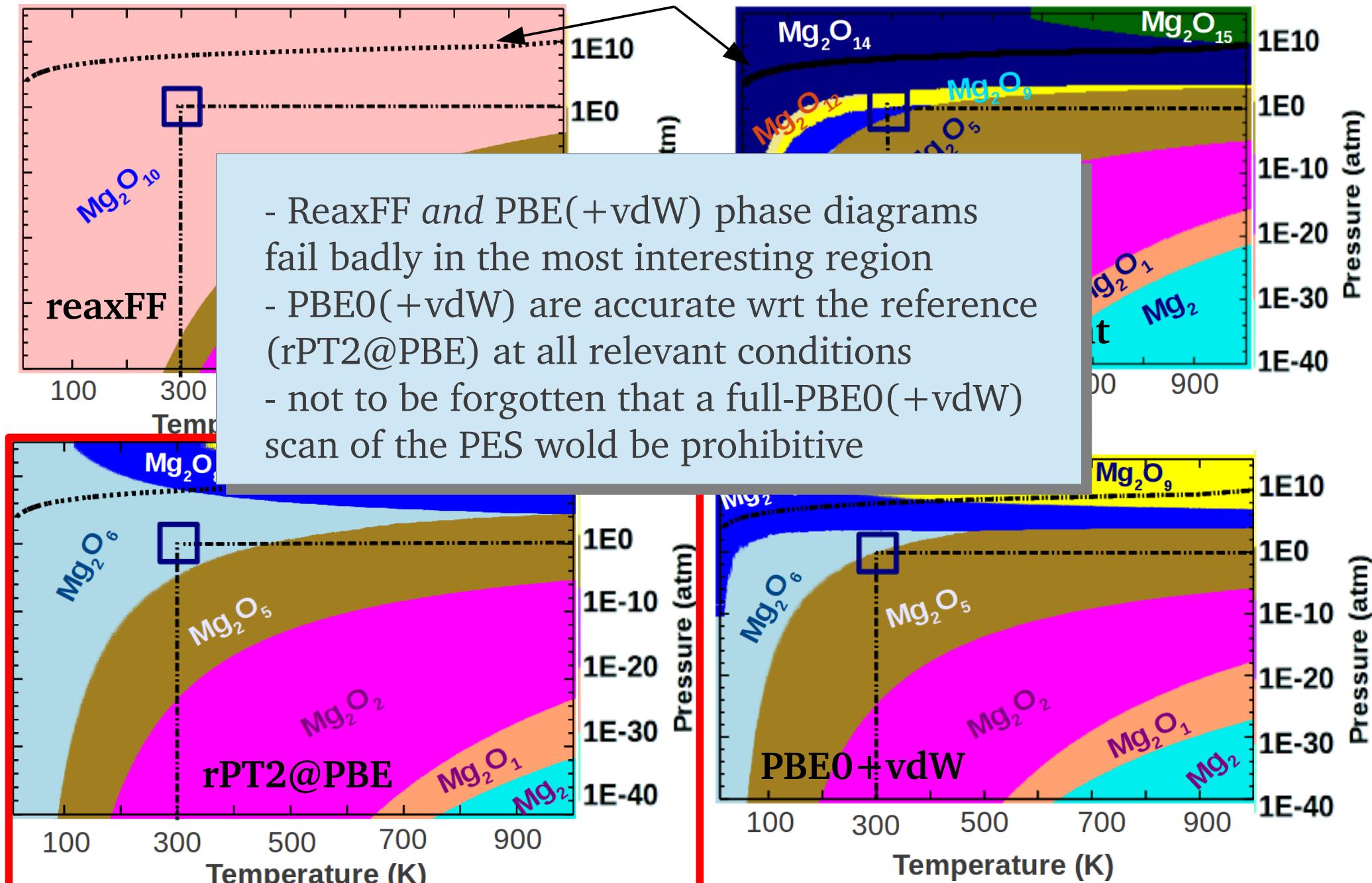
Small clusters are non-stoichiometric (high O coverage)

S. Bhattacharya, S. Levchenko, LMG, and M. Scheffler, PRL (2013)
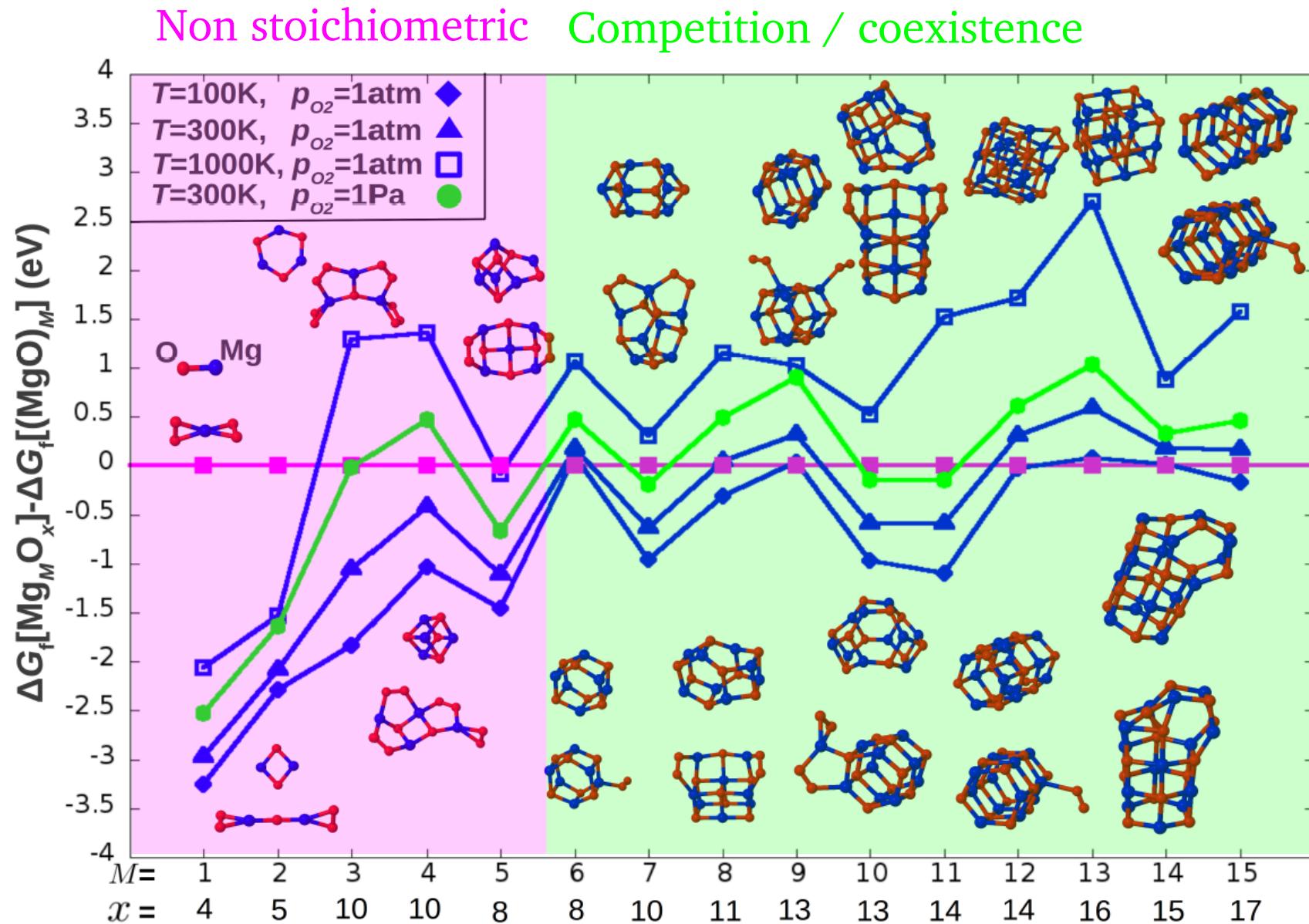
ReaxFF is fairly good for stoich. clusters, fails for the non-stoich.

Mg_MO_x global minima: $1 \leq M \leq 15$

Stoichiometric $(MgO)_M$ clusters
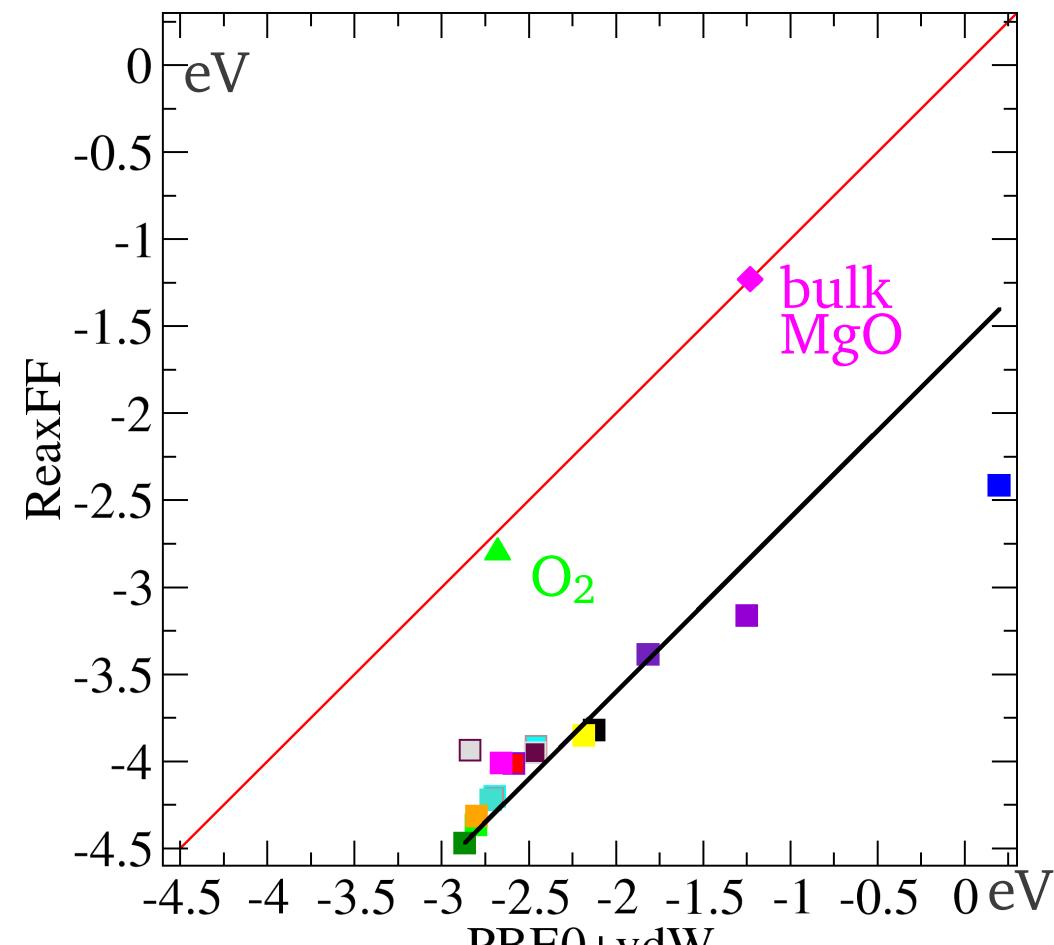
Stoich. + non-stoich. Mg_MO_x clusters

Offset: -1.60 eV   MAE: 0.20 eV

Offset: -1.91 eV   MAE: 0.48 eV
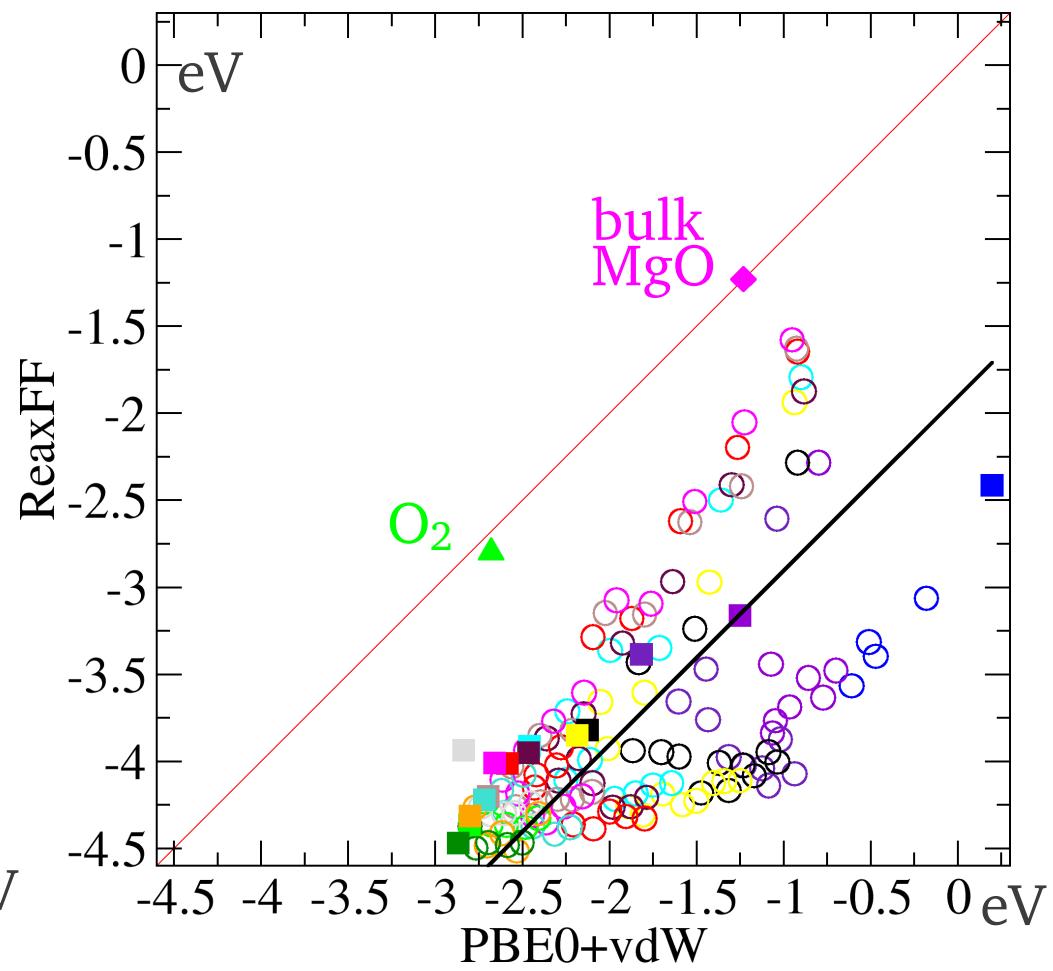
Cohesion/formation energy, referred to atomic Mg and half of O_2 total energy

PBE+vdW is good for stoich. clusters, fails at high O-coverage

Stoichiometric global minima; $1 \leq M \leq 15$

PBE+vdW

0 eV

−0.5

−1

bulk
MgO

−1.5

−2

−2.5

−3

O_2

−3   −2.5   −2   −1.5   −1   −0.5   0 eV
PBE0+vdW
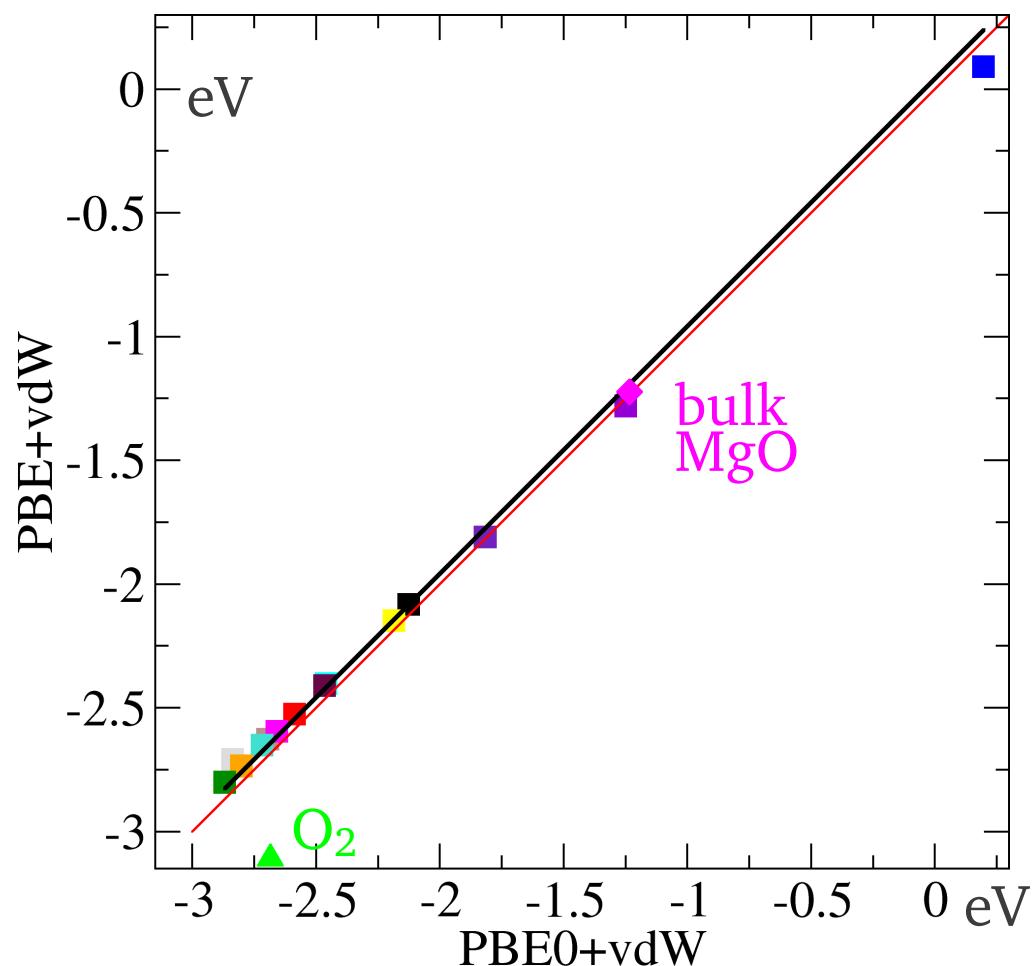
Offset: 0.04 eV
MAE: 0.04 eV

Stoich. and non-stoichiometric global minima; $1 \leq M \leq 3$

PBE+vdW

0 eV

Mg_1O_x

−0.5

Mg_2O_x

−1

Mg_3O_x

−1.5

−1.5   −1   −0.5   0 eV
PBE0+vdW
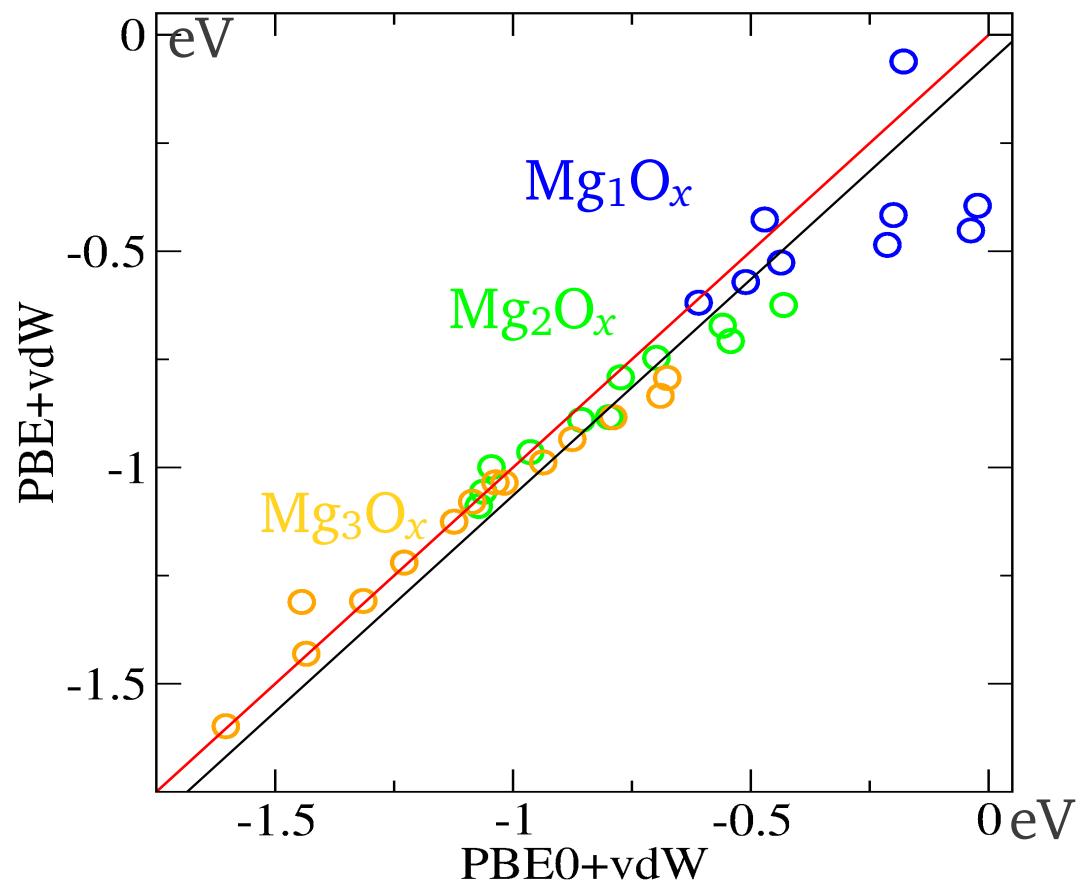
Offset: -0.07 eV
MAE: 0.09 eV

PBE+vdW fails at high O-coverage

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

PBE+vdW / tight

PBE0+vdW

Offset: -0.07 eV
MAE: 0.09 eV
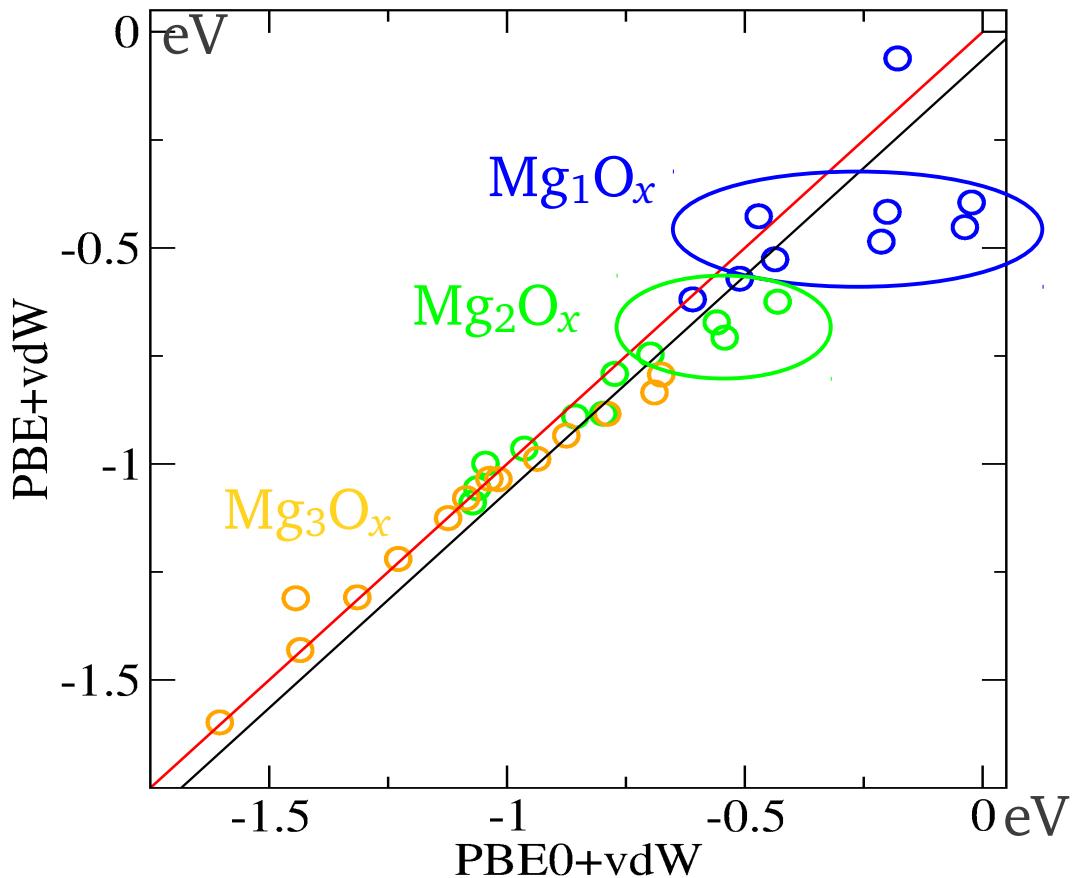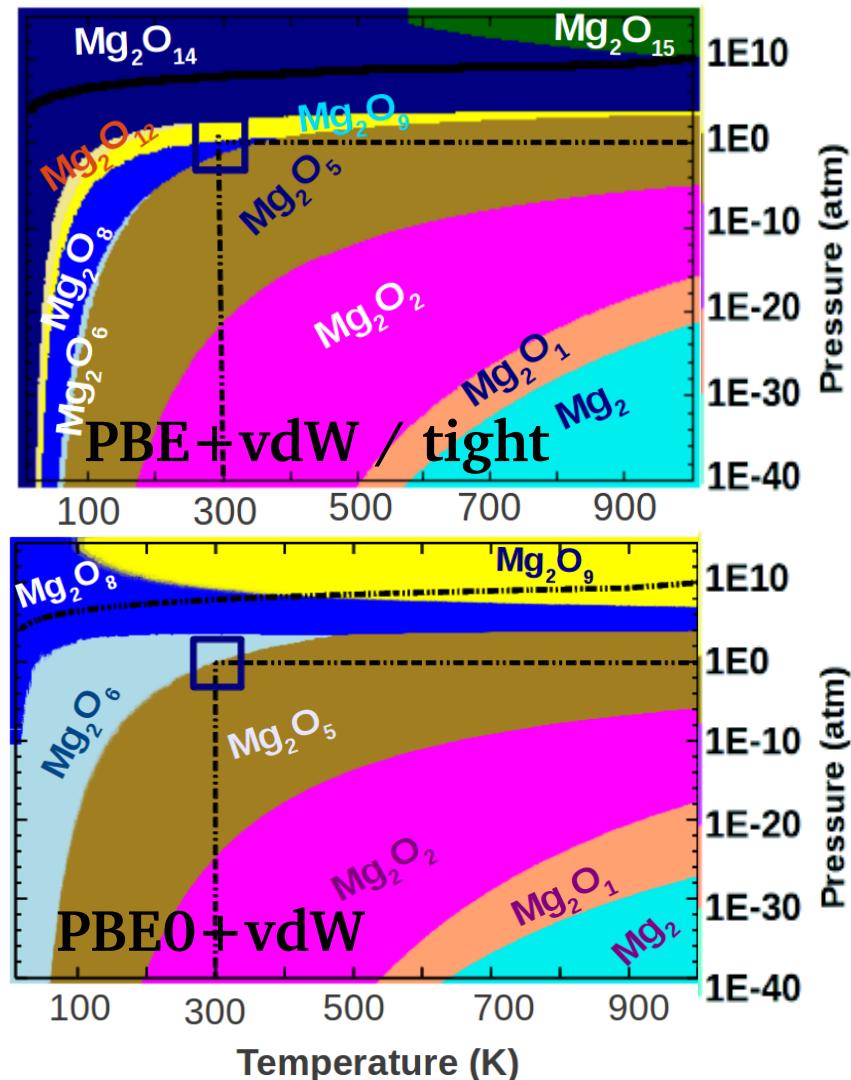
The PBE+vdW phase diagram a higher p is totally unreliable

# DFT as post-production applied to force-field-based GA?

Stoichiometric: Mg_2O_2

Non-stoichiometric: Mg_2O_6
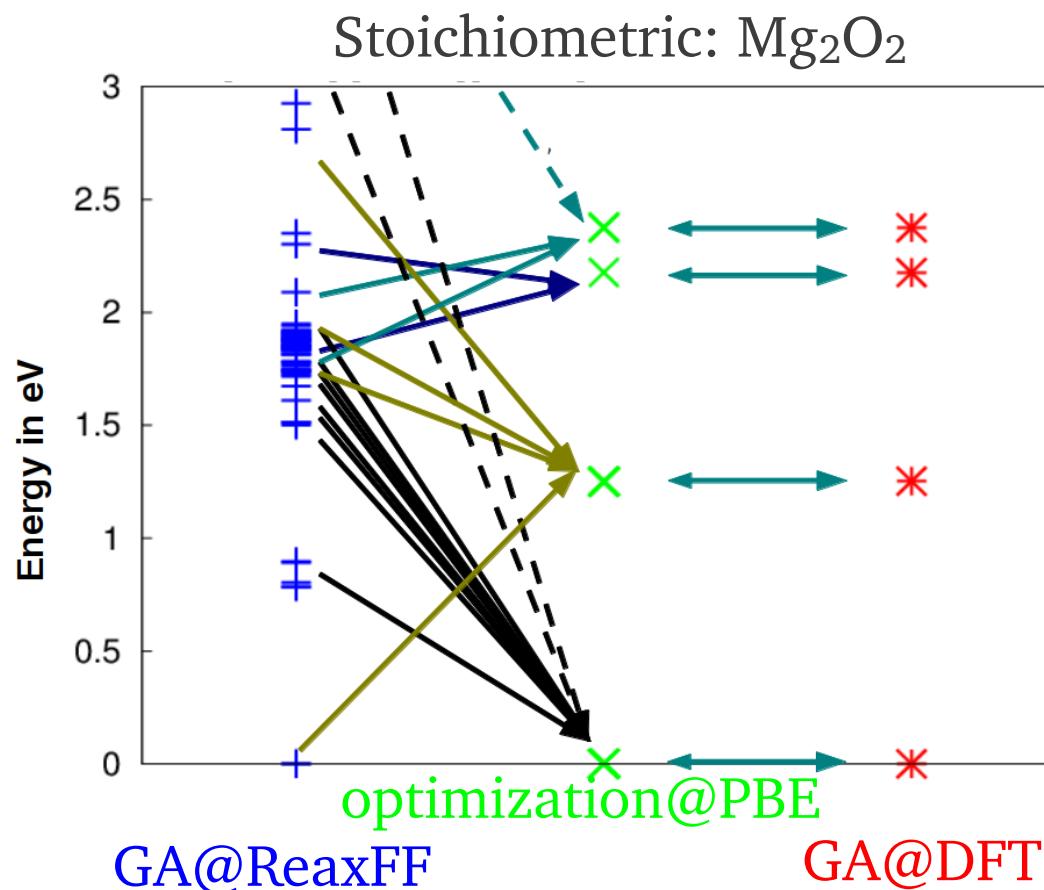
PBE after GA@reaxFF: OK
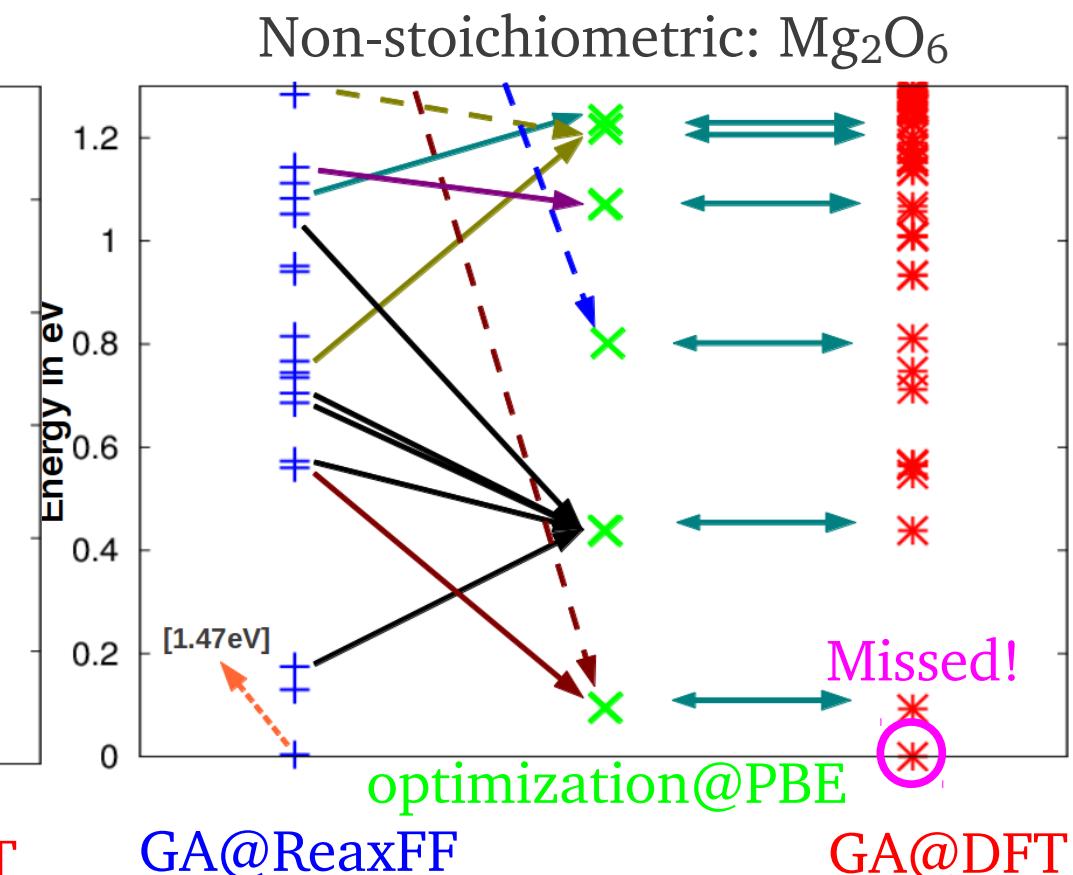
PBE after GA@reaxFF: **GM missed**

Non-stoichiometric: Mg_2O_6

almost same geometry as **C'**

optimization@PBE

GA@ReaxFF

GA@DFT

[1.47eV]
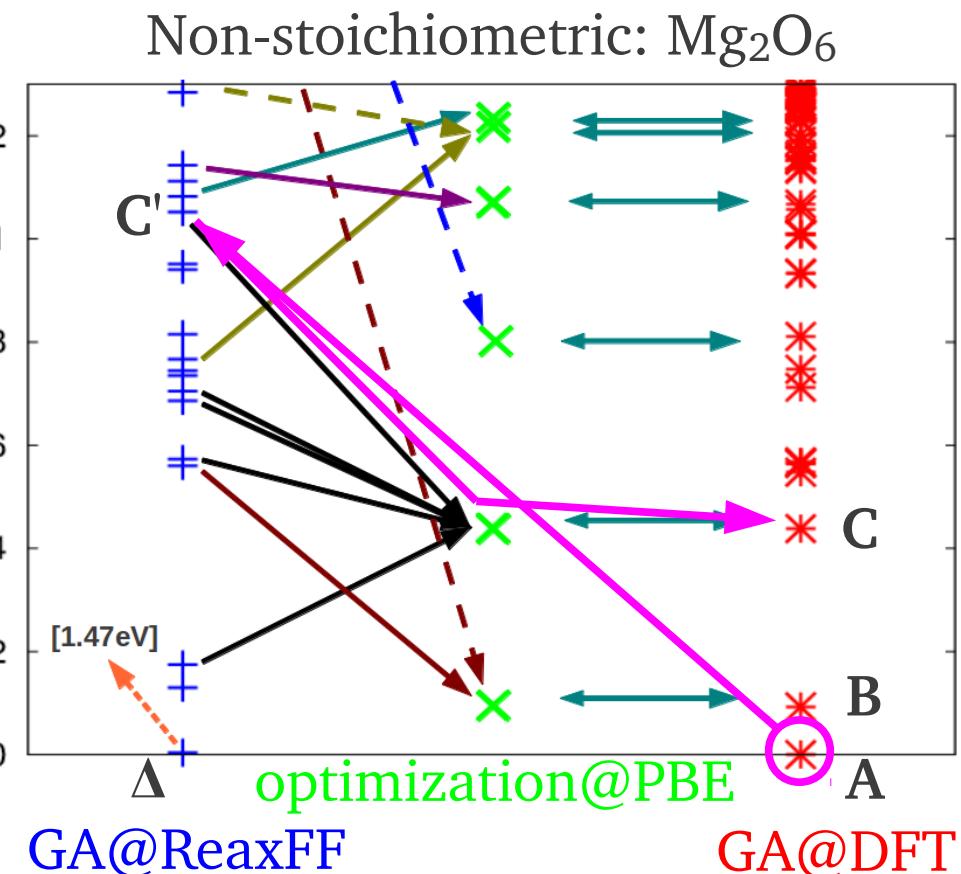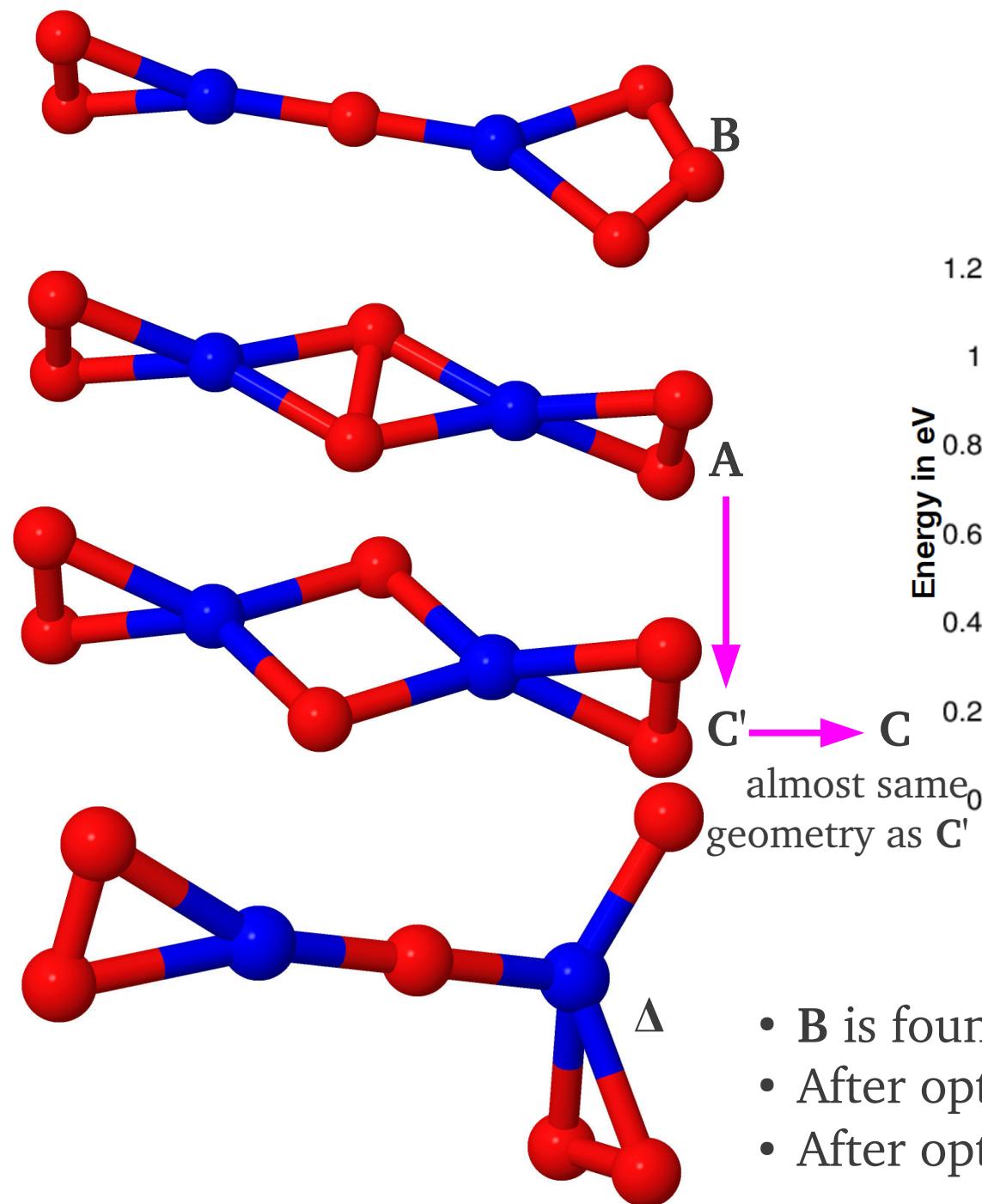
- **B** is found by reaxFF, but not **A**
- After optimization@reaxFF, **A** becomes **C'**
- After optimization@PBE, **C'** becomes **C** ≠ **A**

System in a fluxional
or liquid state:

Ab initio
replica-exchange
molecular dynamics
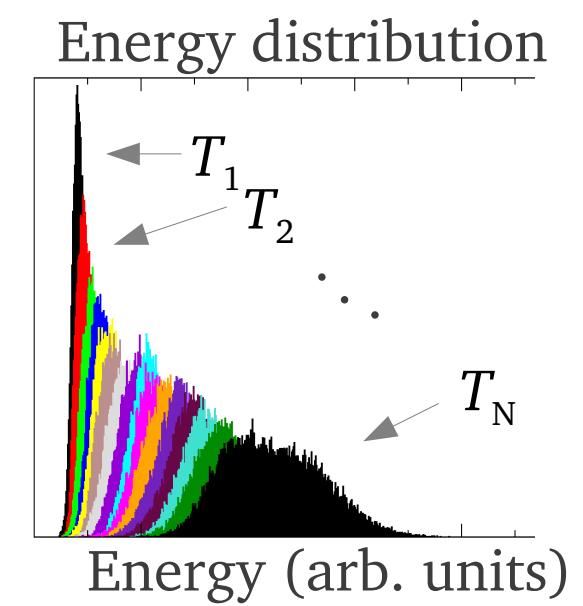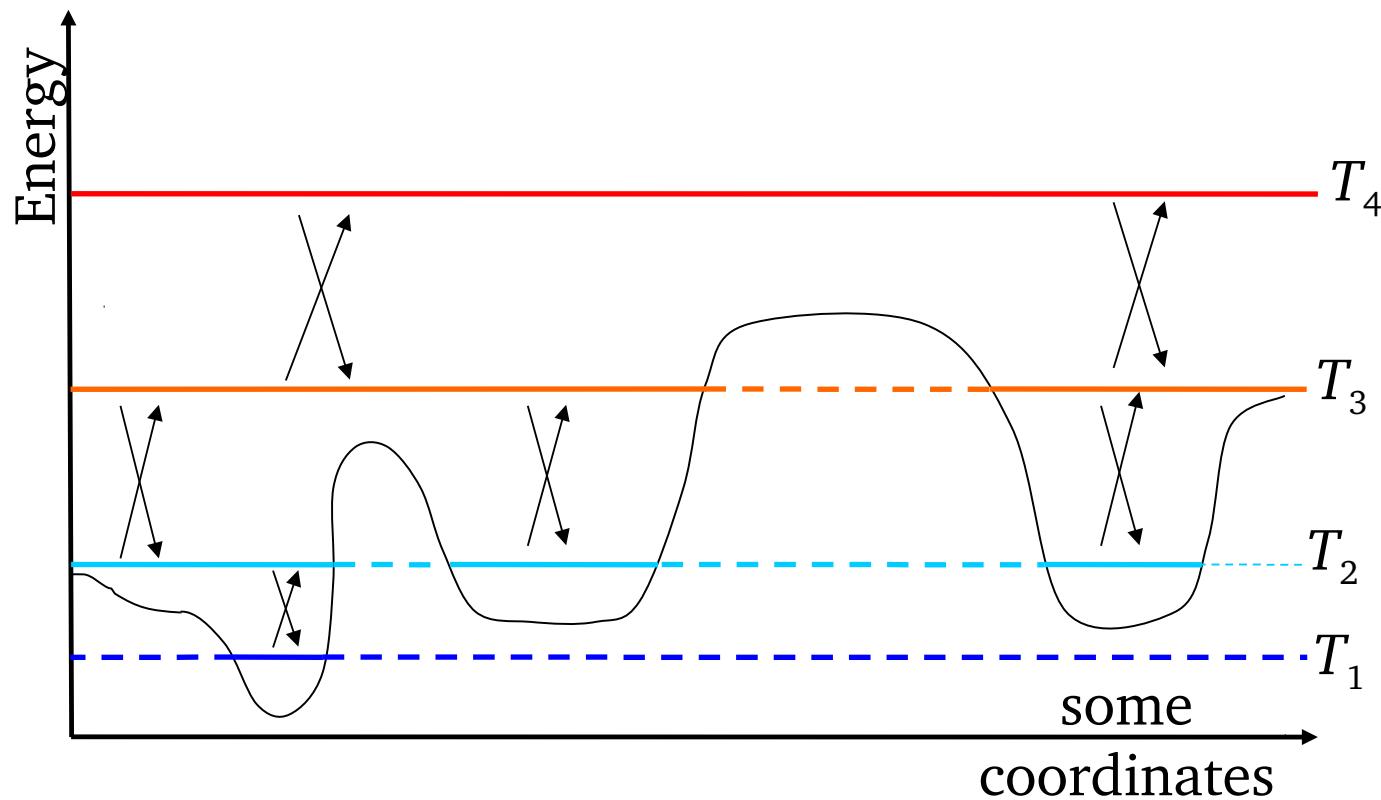
Exchange rule, ensuring canonical sampling at all temperatures:

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

Replica exchange: the implementation
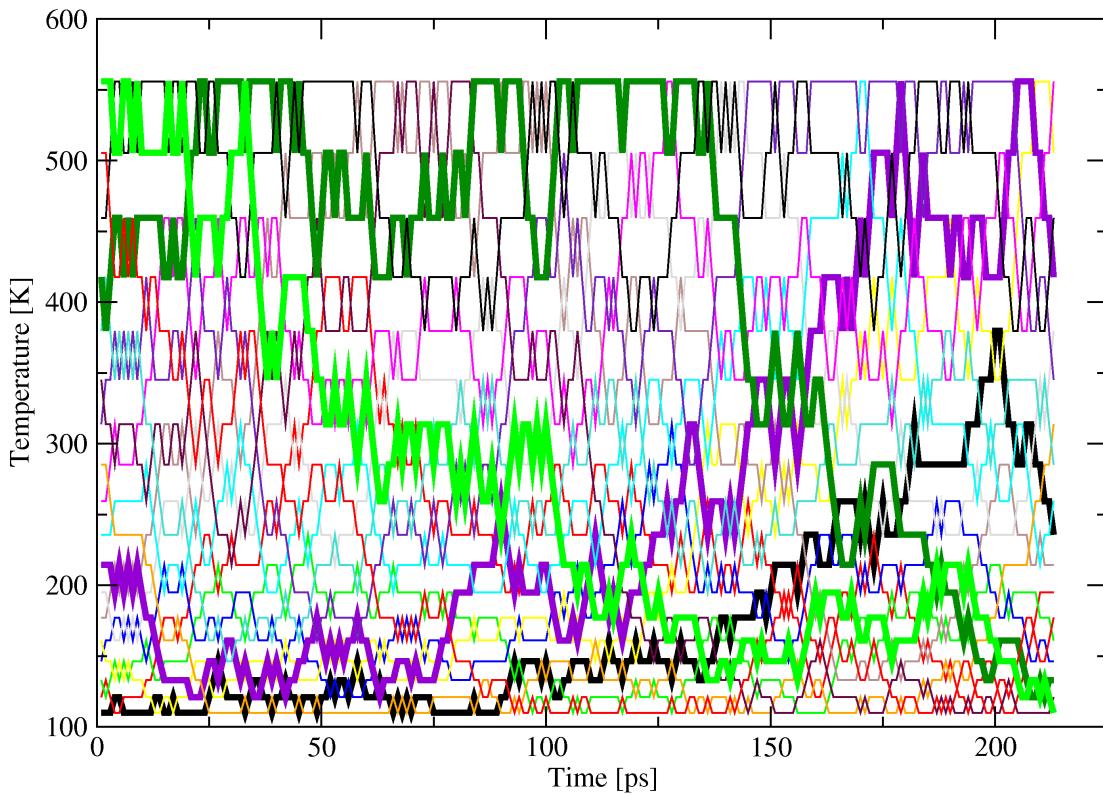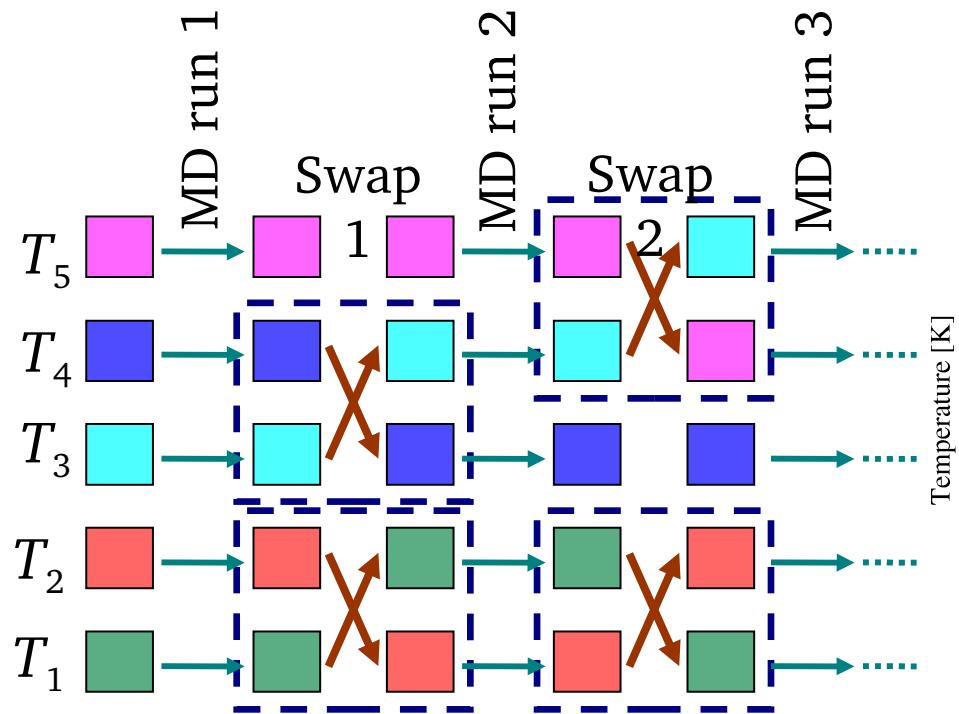
Parameter to be tuned for efficient sampling:
number of temperatures, list of temperatures, attempted swap frequency

0.00 eV

0.04 eV

0.36 eV

100—620 K
100 K PT (100 ps)
100 K serial (100 ps)

Potential Energy (eV)

α (degree)
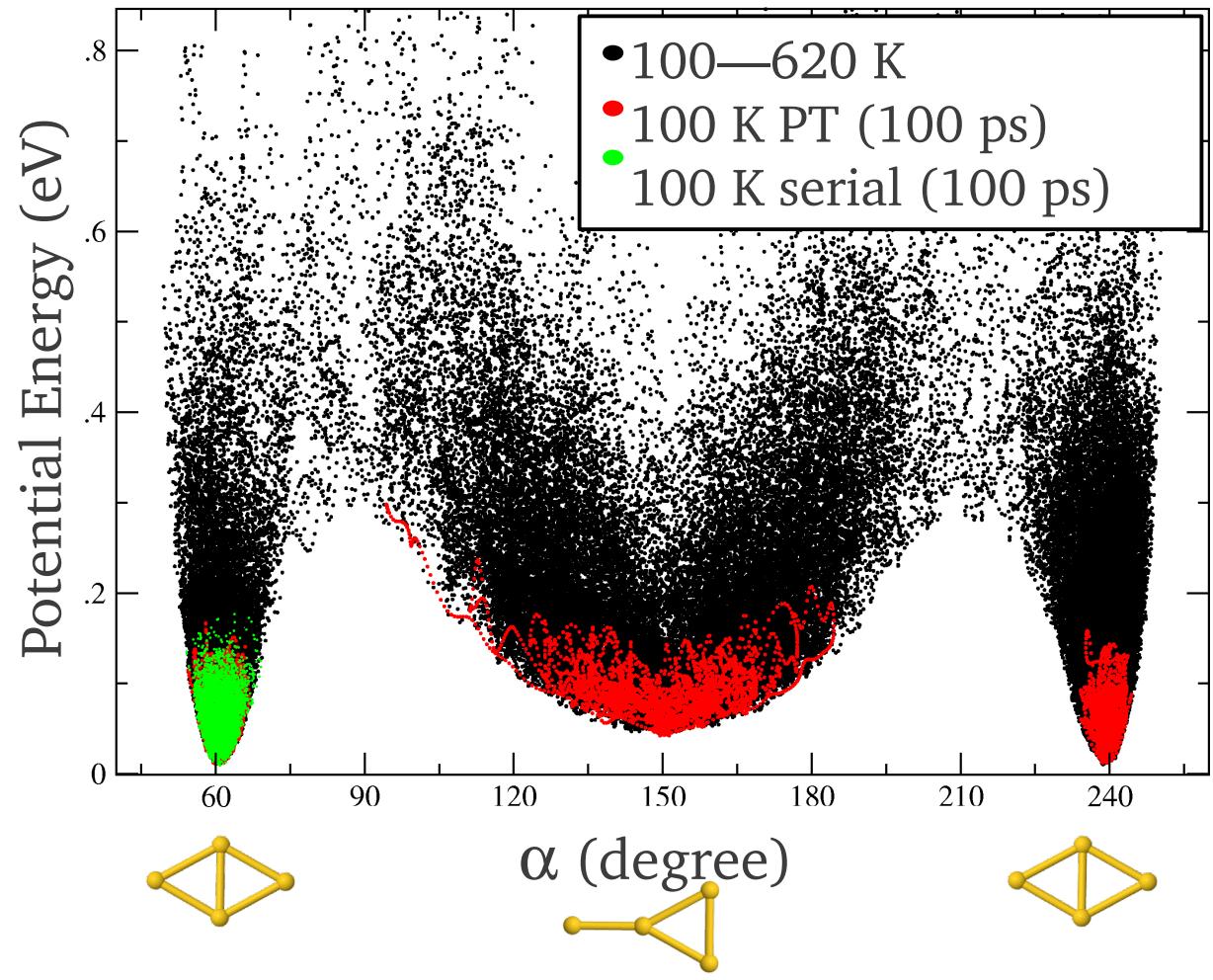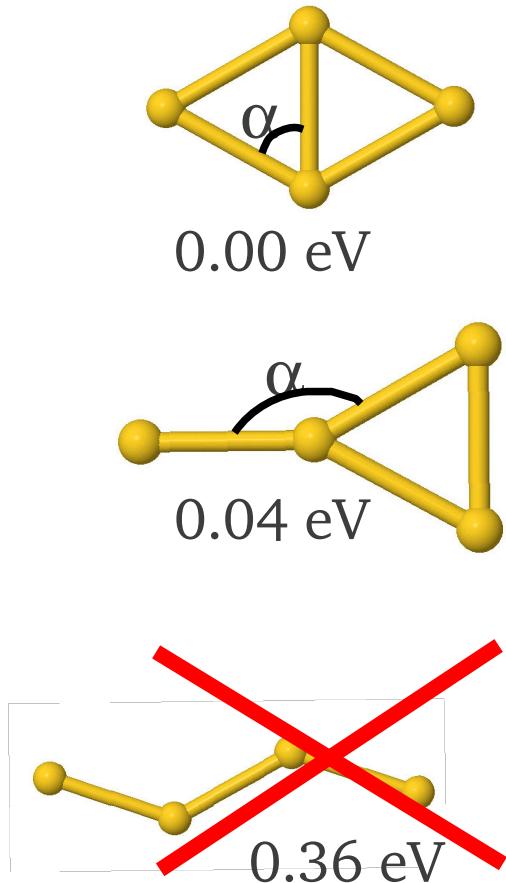
Replica exchange: free energy?

Temperature-weighted Histogram Analysis Method:

Sampled probability   Re-weighting coefficients

Un-biased probability at temperature β_0

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

normalization q is chosen *a posteriori*

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

Iterative, self consistent solution of:

\# of observations of q in bin i

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

\# of 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
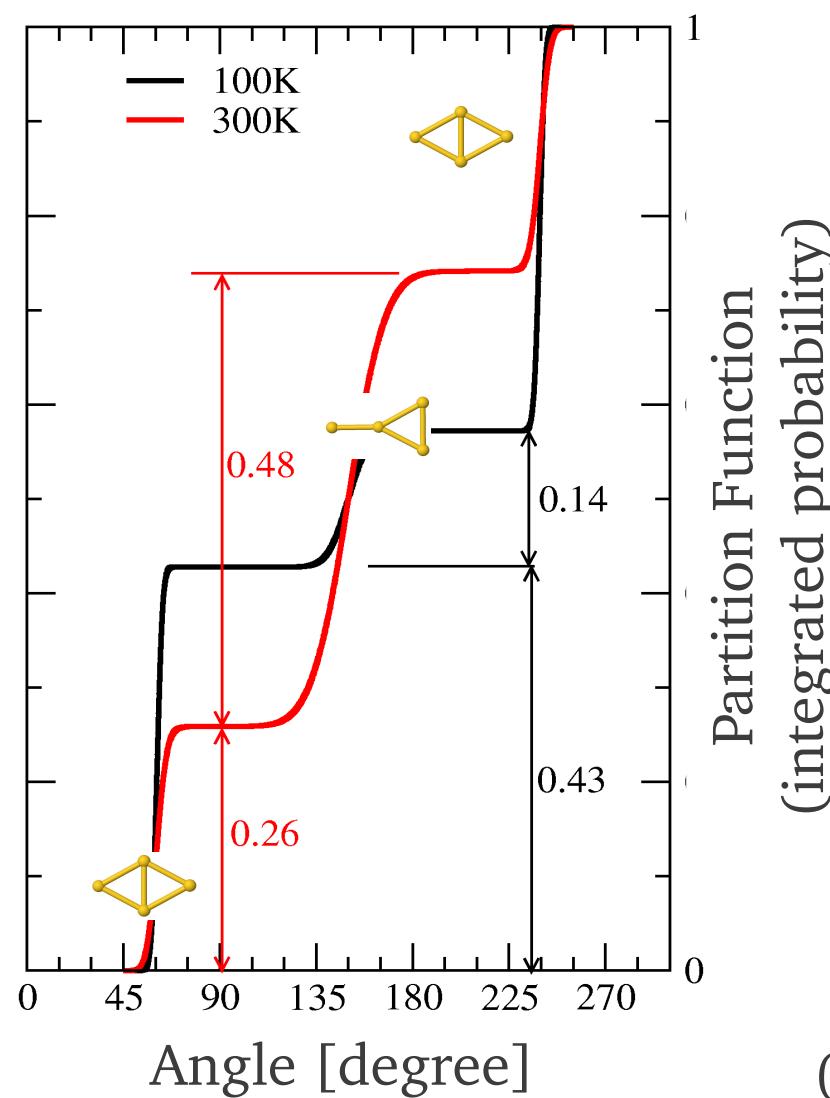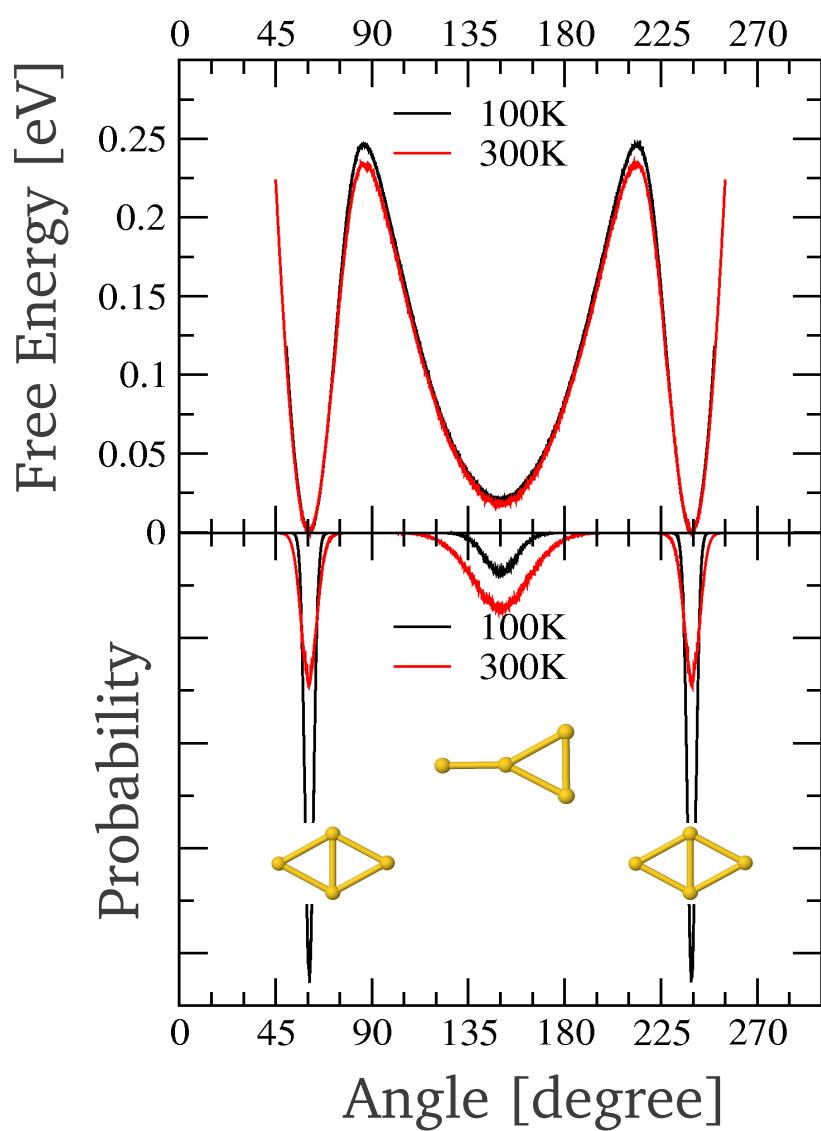
seamlessly multiscale:
bridges vibrational timescale
with state-hopping timescale

$\mathscr{N}$

(ab initio)
replica-exchange
molecular dynamics

unbiased search
for local minima $\mathscr{W}$
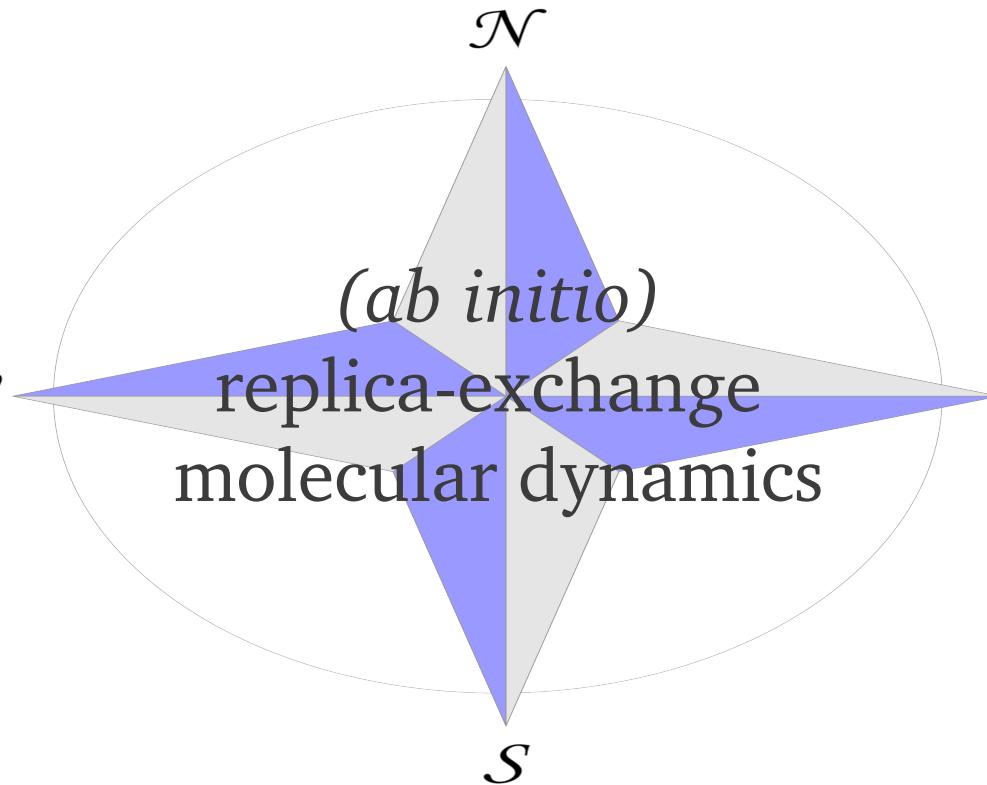
$\mathscr{E}$ *a posteriori*
evaluation of
free-energy
(can be refined)

$\mathscr{S}$

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

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