

# Hands-on workshop ReaxFF Parameterization with the Amsterdam Modeling Suite



Osaka, 30 October 2018

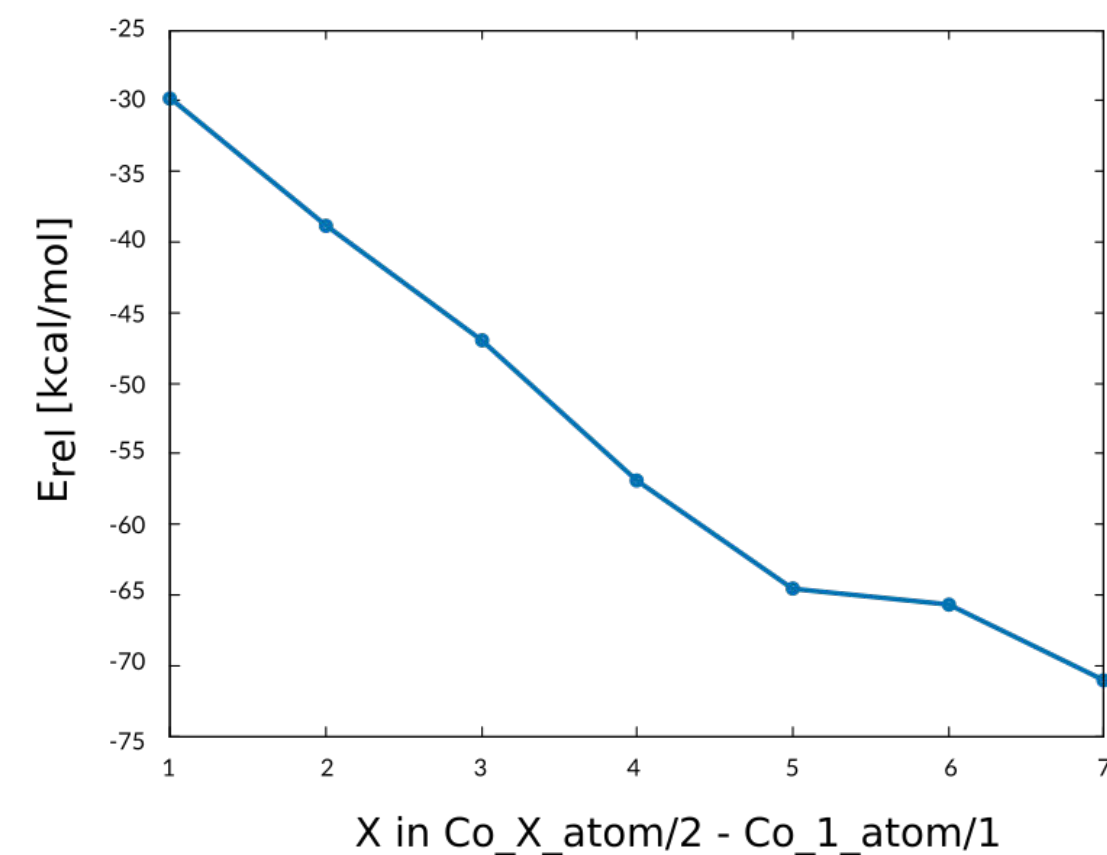
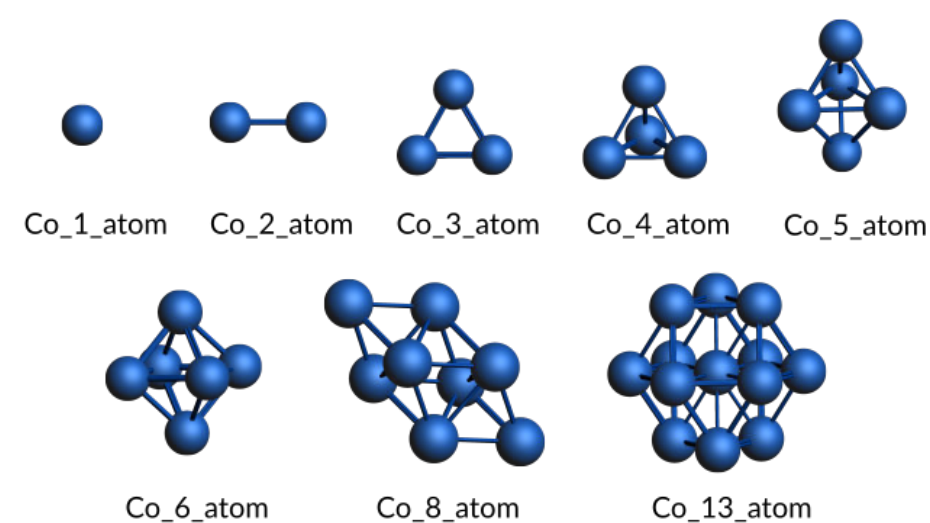
Fedor Goumans, [goumans@scm.com](mailto:goumans@scm.com) SCM support: [support@scm.com](mailto:support@scm.com)

Molsis: [ms-support@molsis.co.jp](mailto:ms-support@molsis.co.jp)

**Making Computational Chemistry Work for You**

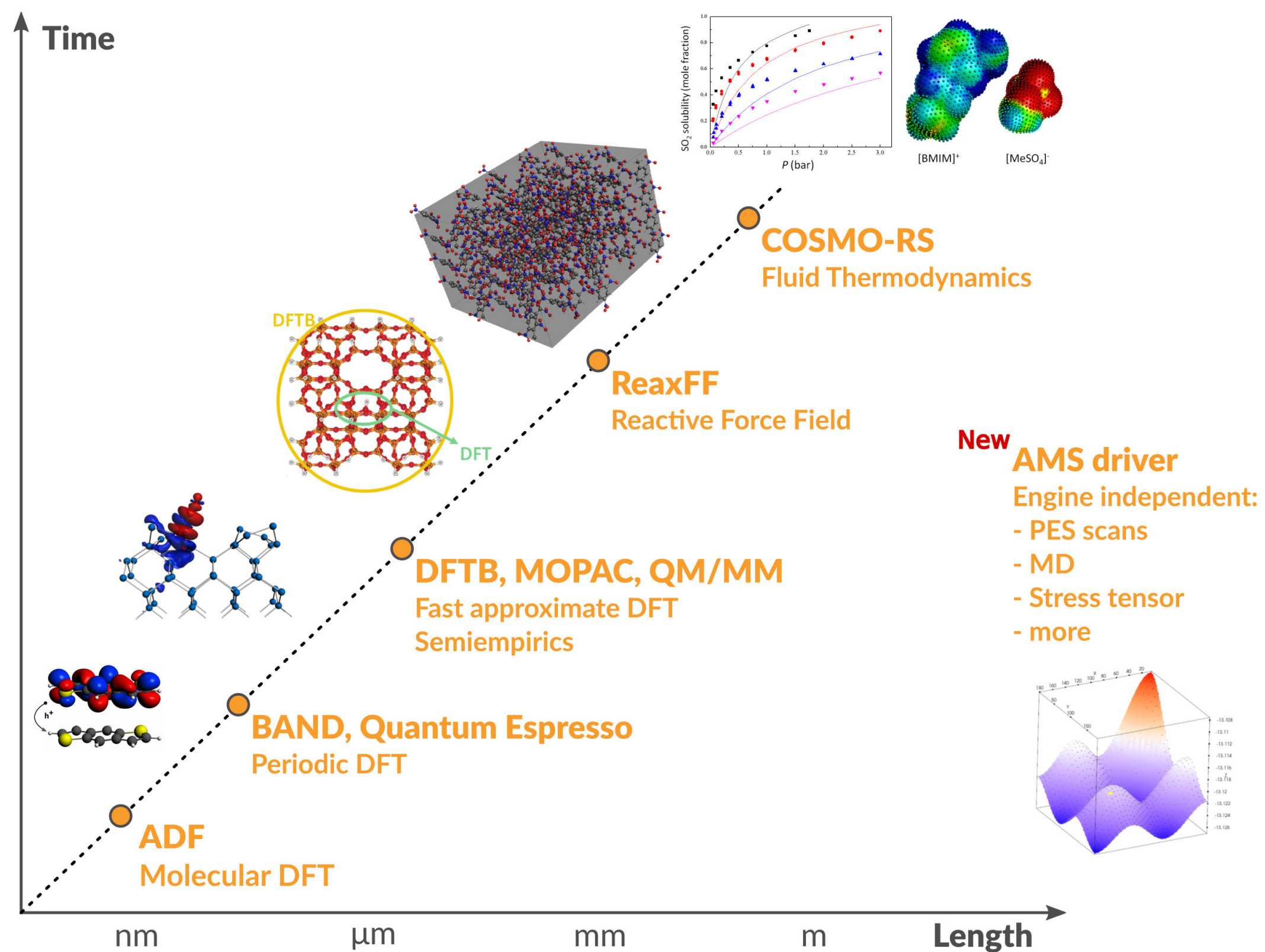
# Program

- Introduction: ReaxFF
  - Some advanced exercises, new features
- Acceleration techniques
  - fbMC, GCMC (thermodynamics), CVHD, bond boost => polymer structures (see slides)
- Refitting a force field for parameterization ([slides](#), [input files](#))
  - Scripting on Windows
  - Adding geometries, conformers, reaction pathways, bond scans
  - Optimizing the force field, checking errors & improving
  - Tips for extending to materials, alloys



# Amsterdam Modeling Suite

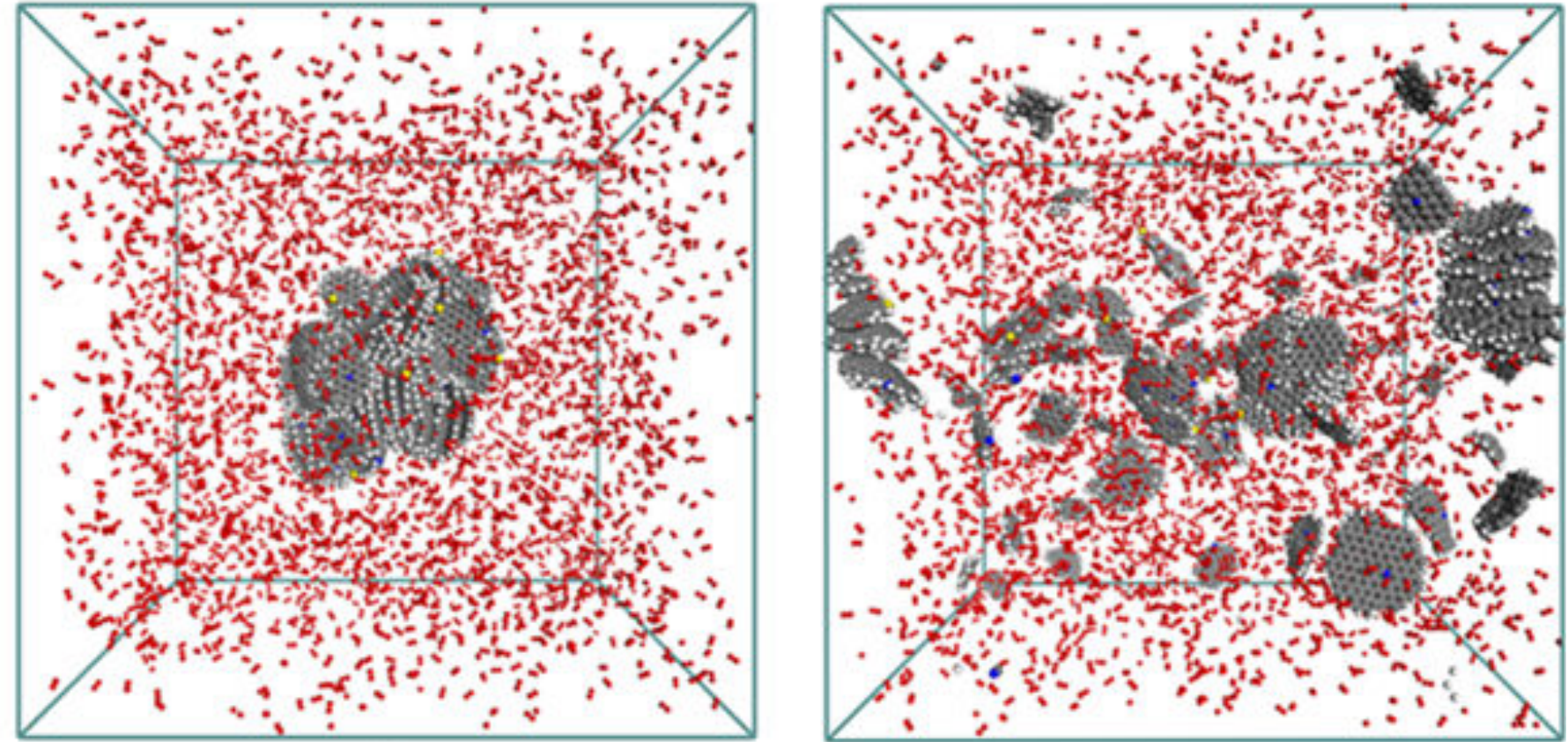
- ADF: powerful molecular DFT
  - Spectroscopy: NMR, EPR, VCD, UV, XAS
  - Advanced solvation / environments
- BAND: periodic DFT
  - (2D) Materials
  - (Orbital) analysis, spectroscopy
- Interface to Quantum ESPRESSO
- DFTB: fast approximate DFT
- ReaxFF: Reactive MD
  - Dynamics of large complicated systems
- COSMO-RS: fluid thermodynamics
  - VLE, LLE, logP, solubility
- Integrated GUI – use out of the box
- Scripting: workflows & automation





# Computational Chemistry & Materials

$$d^2x/dt^2 = F(x)$$
$$F(x) = - dV(x)/dx$$



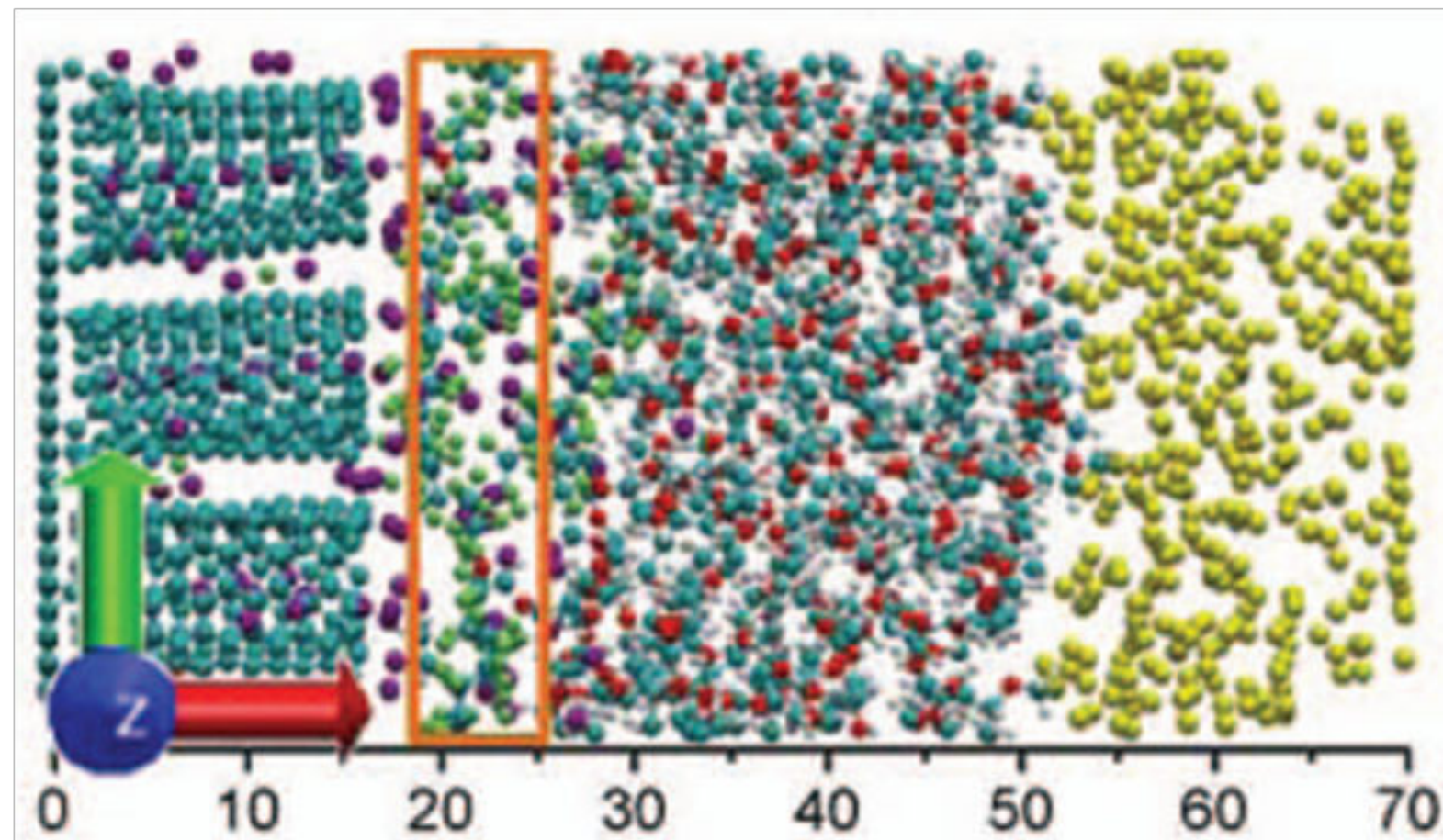
**Molecular dynamics: Newton's equations of motion**

**Movement of atoms: solve numerically + propagate,**

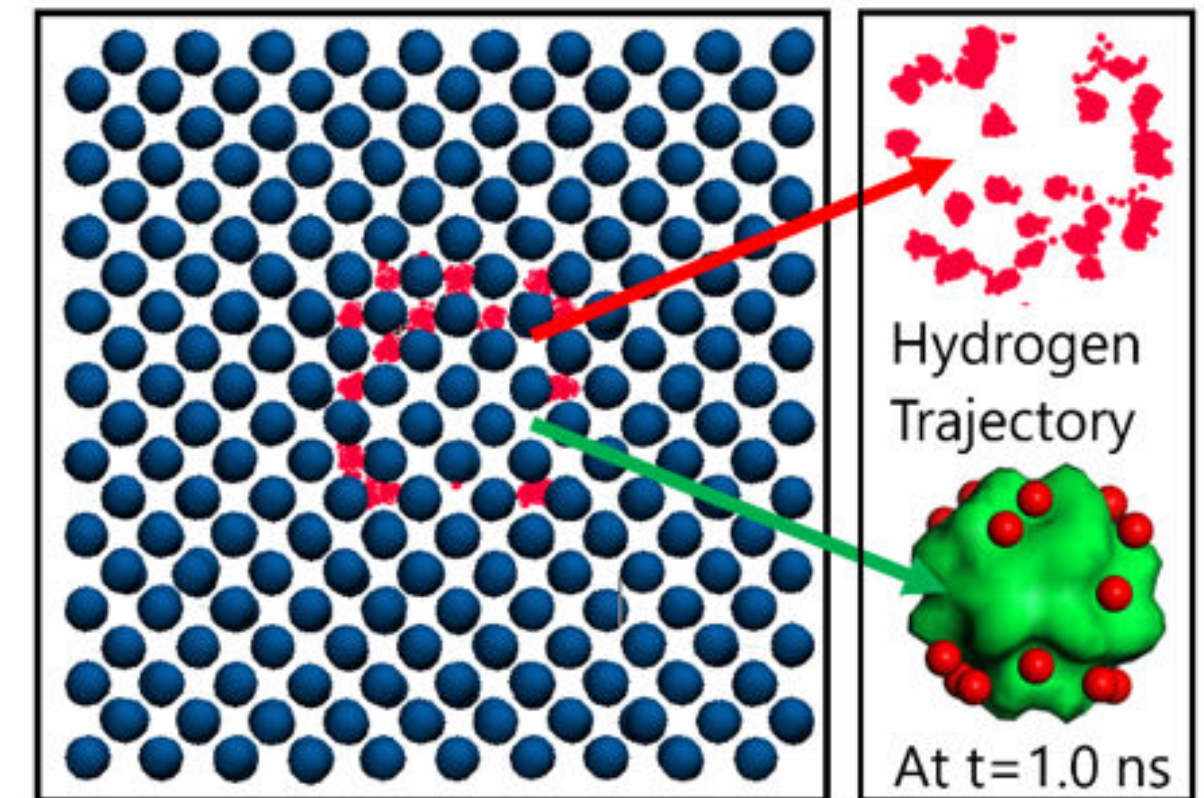
**Properties: reaction rates, diffusion coefficients, stress-strain, ....**



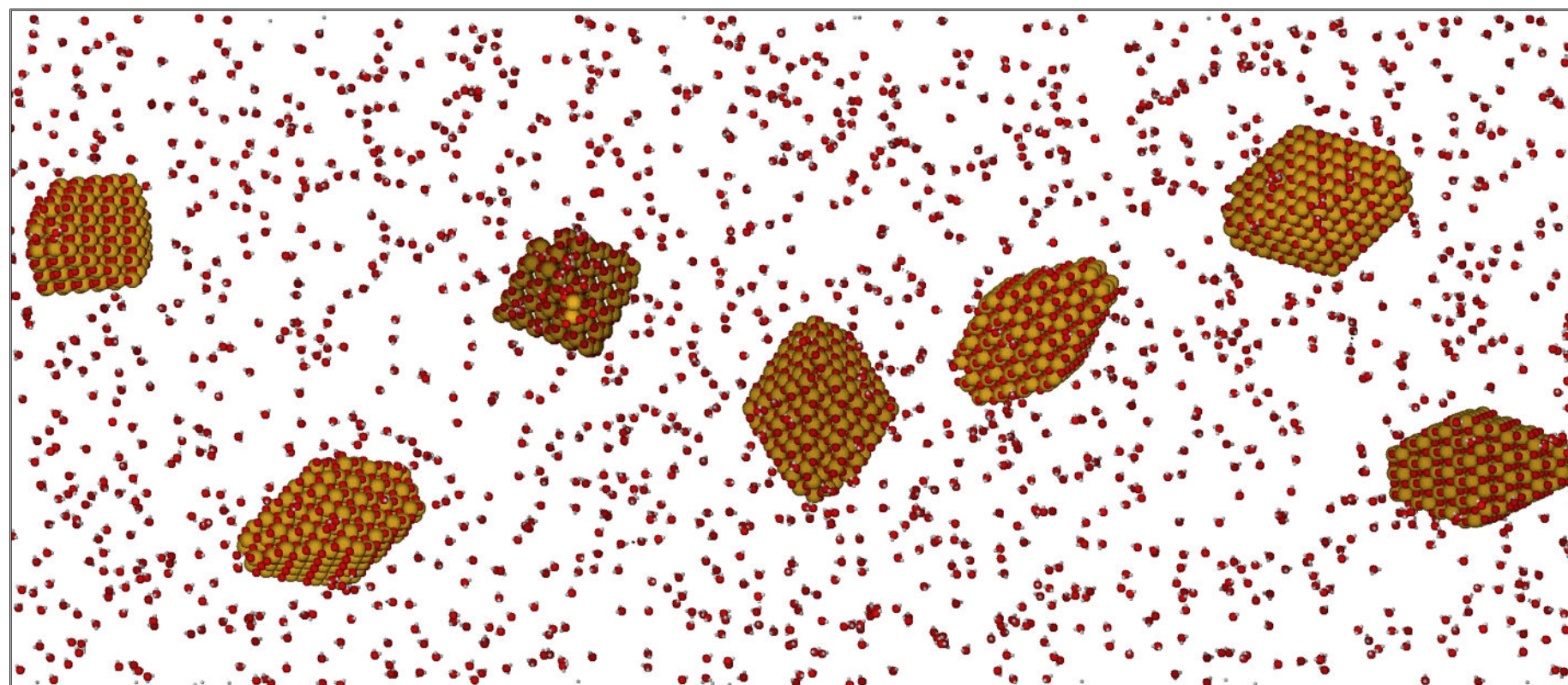
# ReaxFF – reactive molecular dynamics



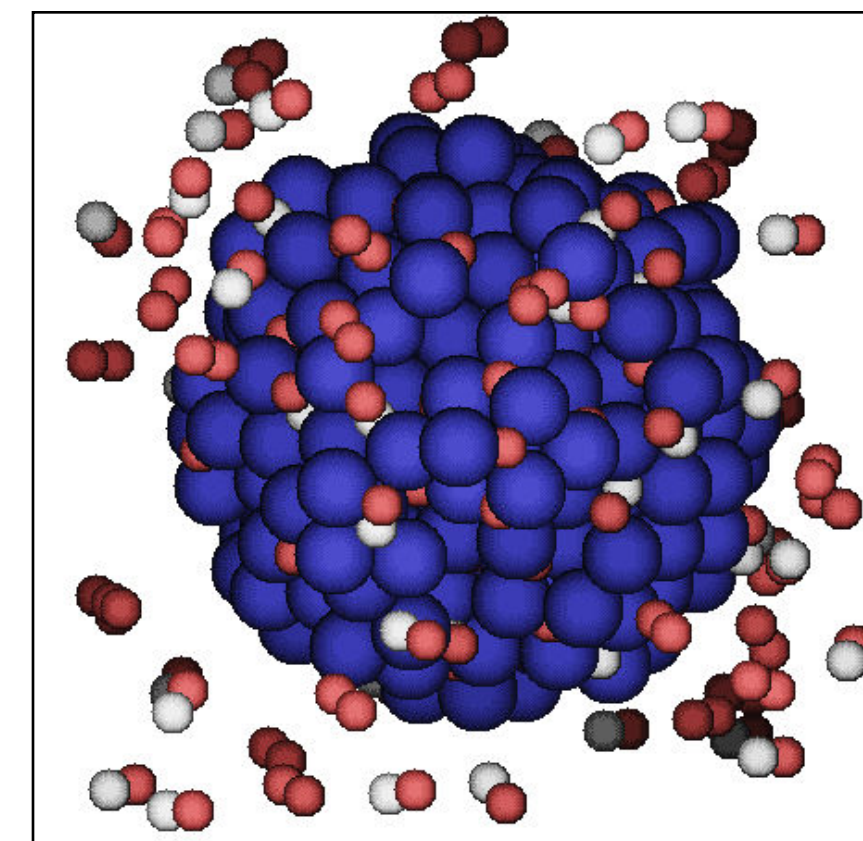
Li battery discharge: *J. Electrochem. Soc.* **161**, E3009 (2014); *PCCP*, **17**, 3383 (2015)



Hydrogen embrittlement of steels  
*Phys. Chem. Chem. Phys.* **18** 761-771 (2016)



Crystallization  $\text{TiO}_2$  nano-particles in water  
[Nano Lett.](#) **14**, 1836-1842 (2014)



Pd-catalysed CO oxidation GCMC+ReaxFF  
*J. Chem. Phys.*, **139** 044109 (2013)

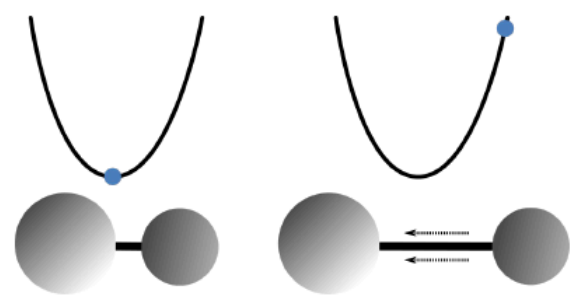


# ReaxFF: introduction

- Simulate complex systems at realistic scales
  - Atomistic potentials: bond orders + charge update

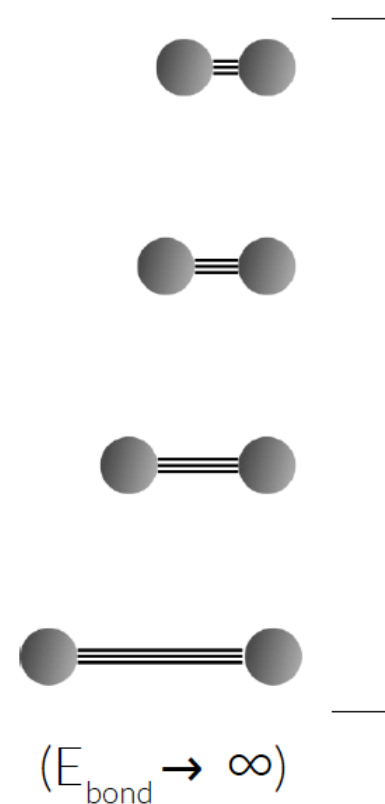
A.C.T. van Duin et al, J. Phys. Chem. A 2001, 105, 9396-9409.

Standard forcefields



Harmonic potentials based on atom distance, bond breaking impossible, e.g.

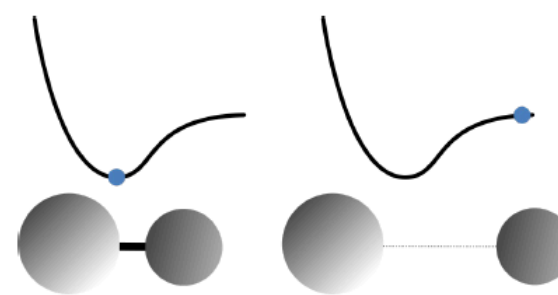
$$E_{\text{bond}} \propto (\text{distance})^2$$



a triple "bond" will always stay a triple "bond"...

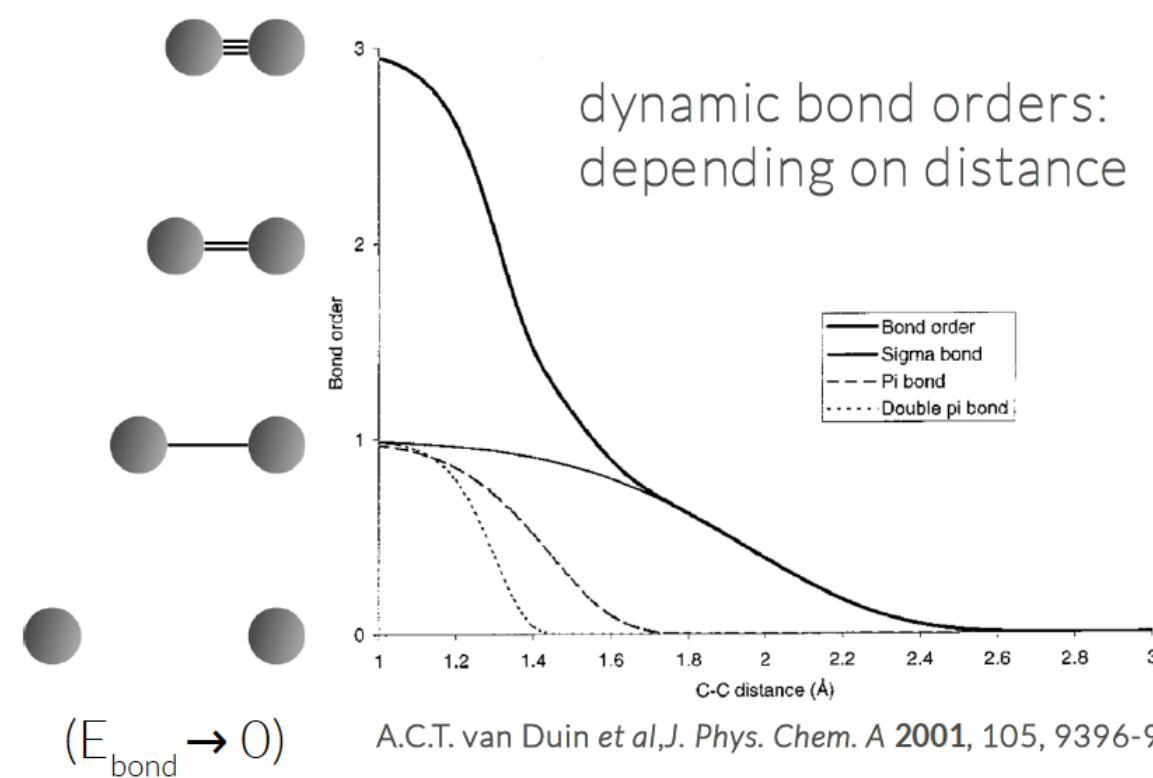
vs

ReaxFF



Non-harmonic potentials based on bond orders, bond breaking/forming possible, e.g.

$$E_{\text{bond}} \propto -(\text{bond order}) \times \exp[ (1 - \text{bond order}) ]$$



[See ReaxFF intro slides](#)

# General ReaxFF rules

- No discontinuities in energy or forces
- No pre-defined reaction sites or types
- Only 1 atom type per element

$$E_{\text{system}} = E_{\text{bond}} + E_{\text{lp}} + E_{\text{over}} + E_{\text{under}} + E_{\text{val}} + E_{\text{pen}} + E_{\text{coa}} + E_{\text{C}_2} + E_{\text{tors}} + E_{\text{conj}} + E_{\text{H-bond}} + E_{\text{vdWaals}} + E_{\text{Coulomb}}$$

$$\text{BO}'_{ij}(r_{ij}) = \exp \left[ \rho_{\text{bo},1} \cdot \left( \frac{r_{ij}}{r_o} \right)^{\rho_{\text{bo},2}} \right] + \exp \left[ \rho_{\text{bo},3} \cdot \left( \frac{r_{ij}^{\pi}}{r_{o,\pi}} \right)^{\rho_{\text{bo},4}} \right] + \exp \left[ \rho_{\text{bo},5} \cdot \left( \frac{r_{ij}^{\pi\pi}}{r_{o,\pi\pi}} \right)^{\rho_{\text{bo},6}} \right]$$

In: distance between atoms,  $r_{ij}$

Out: 1, 2, 1.42, etc...

Parameters = 16

$\rho_{\text{bo},1}, \rho_{\text{bo},2}, \rho_{\text{bo},3}, \rho_{\text{bo},4}, \rho_{\text{bo},5}, \rho_{\text{bo},6}, r_o, r_{o,\pi}, r_{o,\pi\pi}$   
 $\text{val}_1, \text{val}_2, \lambda_1, \lambda_2, \lambda_3, \lambda_4, \lambda_5$

Correction terms  $f_1, f_2, f_3$ :  $\text{BO}_{ij}(r_{ij}) = \text{BO}'_{ij}(r_{ij}) \cdot f_1(\text{BO}'_{ij}) \cdot f_2(\text{BO}'_{ij}) \cdot f_3(\text{BO}'_{ij})$

# ReaxFF parameters, transferability

- many elements studied
- each pair needs bonded terms
- validate force field

- GUI checks
- training data crucial
- application specific

- New parameters

- ADF 2013: 17 sets, 19 elements
- ADF 2014: 38 sets, 29 elements
- ADF 2016: 58 sets, 38 elements
- ADF 2017: 79 sets, 38 elements
- AMS2018: 81 sets, 40 elements + Ho/EI
- van Duin, Goddard, others
- RxFF consulting
- [MCFF & CMA-ES](#) parameterization

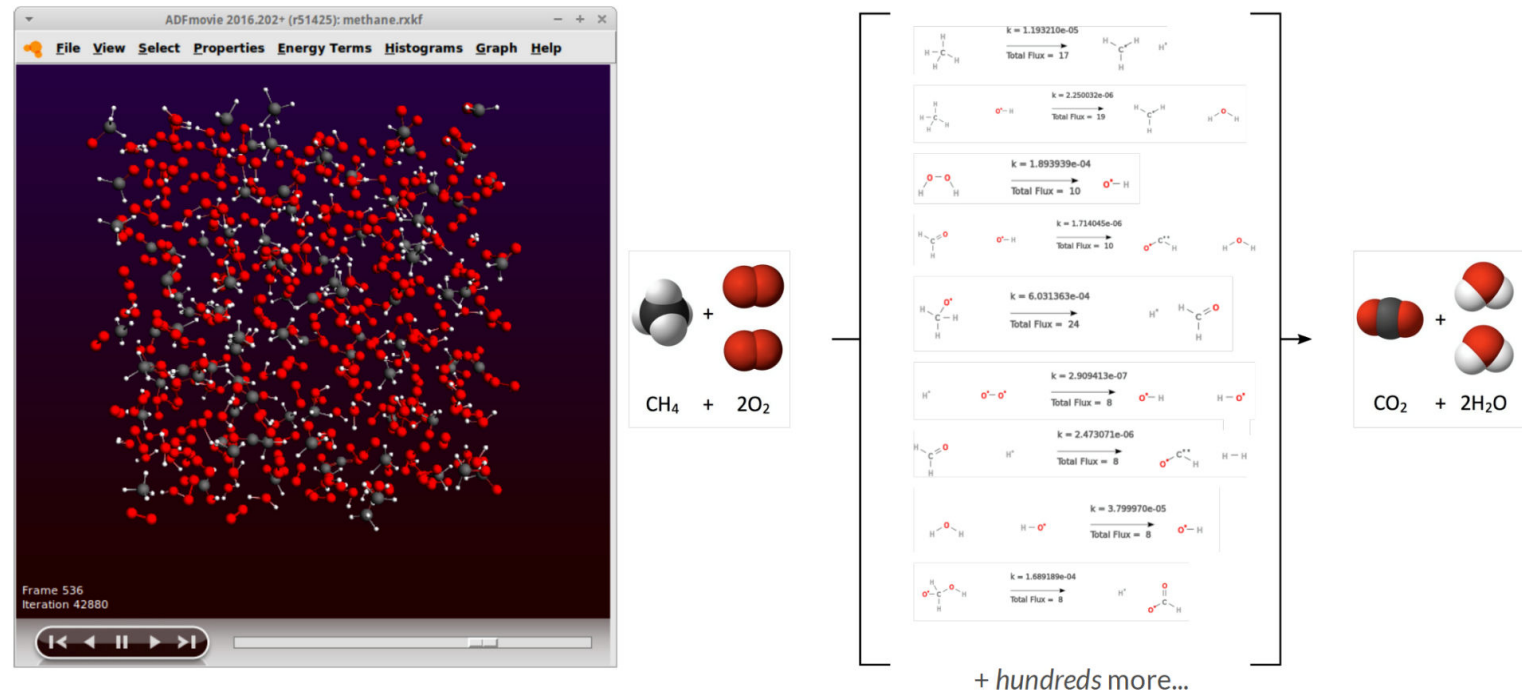
**Available**  
**Not yet available**

1 H hydrogen																				2 He helium						
3 Li lithium	4 Be beryllium																				5 B boron	6 C carbon	7 N nitrogen	8 O oxygen	9 F fluorine	10 Ne neon
11 Na sodium	12 Mg magnesium																				13 Al aluminum	14 Si silicon	15 P phosphorus	16 S sulfur	17 Cl chlorine	18 Ar argon
19 K potassium	20 Ca calcium	21 Sc scandium	22 Ti titanium	23 V vanadium	24 Cr chromium	25 Mn manganese	26 Fe iron	27 Co cobalt	28 Ni nickel	29 Cu copper	30 Zn zinc	31 Ga gallium	32 Ge germanium	33 As arsenic	34 Se selenium	35 Br bromine	36 Kr krypton									
37 Rb rubidium	38 Sr strontium	39 Y yttrium	40 Zr zirconium	41 Nb niobium	42 Mo molybdenum	43 Tc technetium	44 Ru ruthenium	45 Rh rhodium	46 Pd palladium	47 Ag silver	48 Cd cadmium	49 In indium	50 Sn tin	51 Sb antimony	52 Te tellurium	53 I iodine	54 Xe xenon									
55 Cs cesium	56 Ba barium	57-71 lanthanide	72 Hf hafnium	73 Ta tantalum	74 W tungsten	75 Re rhenium	76 Os osmium	77 Ir iridium	78 Pt platinum	79 Au gold	80 Hg mercury	81 Tl thallium	82 Pb lead	83 Bi bismuth	84 Po polonium	85 At astatine	86 Rn radon									
87 Fr francium	88 Ra radium	89-103 actinide	104 Rf rutherfordium	105 Db dubnium	106 Sg seaborgium	107 Bh bohrium	108 Hs hassium	109 Mt meitnerium	110 Ds darmstadtium	111 Rg roentgenium	112 Cn copernicium	113 Nh nihonium	114 Fl flerovium	115 Mc moscovium	116 Lv livermorium	117 Ts tennessine	118 Og oganeson									
89 La lanthanum	90 Ce cerium	91 Pr praseodymium	92 Nd neodymium	93 Pm promethium	94 Sm samarium	95 Eu europium	96 Gd gadolinium	97 Tb terbium	98 Dy dysprosium	99 Ho holmium	100 Er erbium	101 Tm thulium	102 Yb ytterbium	103 Lu lutetium												
101 Ac actinium	102 Th thorium	103 Pa protactinium	104 U uranium	105 Np neptunium	106 Pu plutonium	107 Am americium	108 Cm curium	109 Bk berkelium	110 Cf californium	111 Es einsteinium	112 Fm fermium	113 Md mendelevium	114 No nobelium	115 Lr lawrencium												



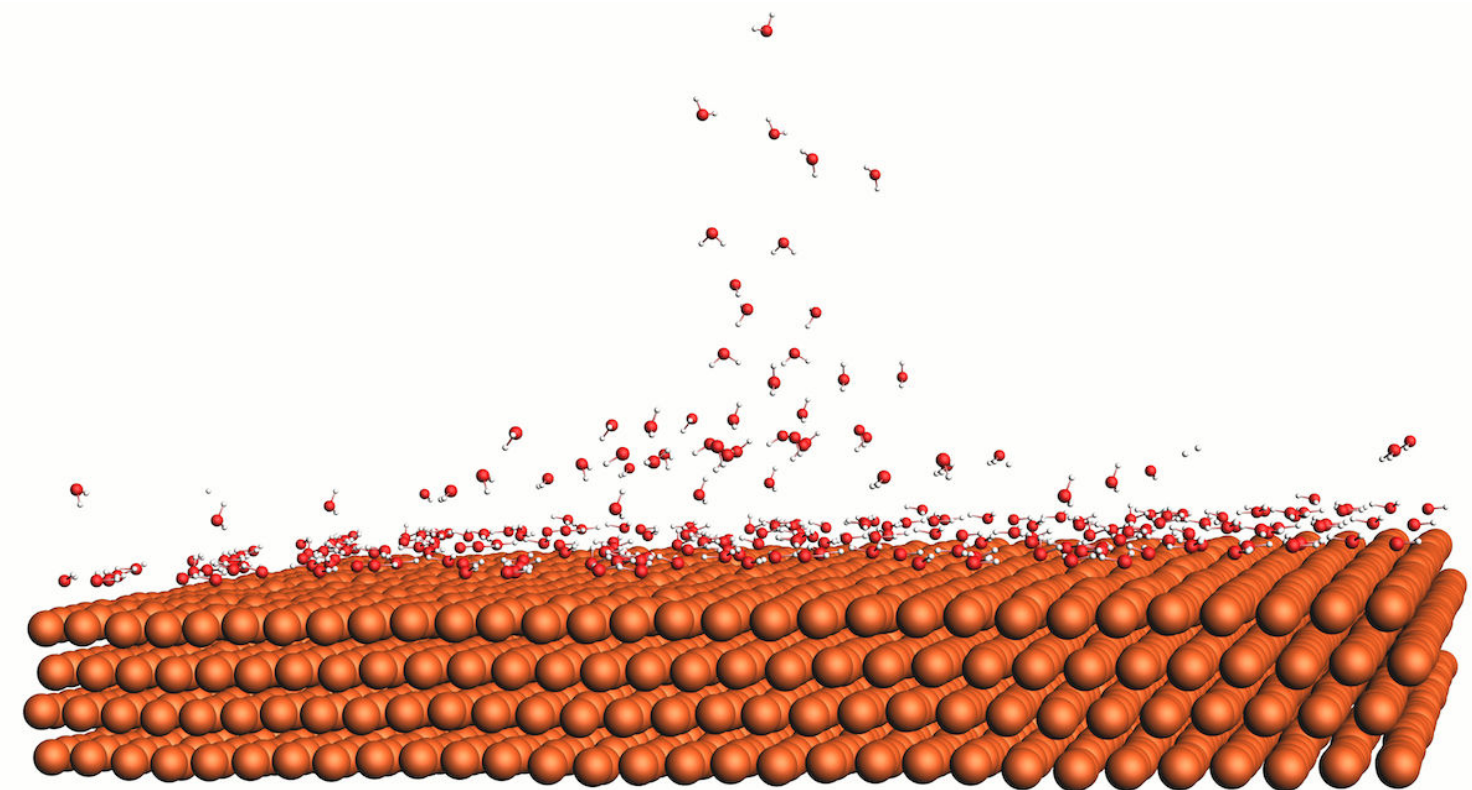
# ReaxFF tools in Amsterdam Modeling Suite

ChemTraYzer: [Automated rates & pathways](#)  
 New in 2018: [Analyze surface reactions](#)



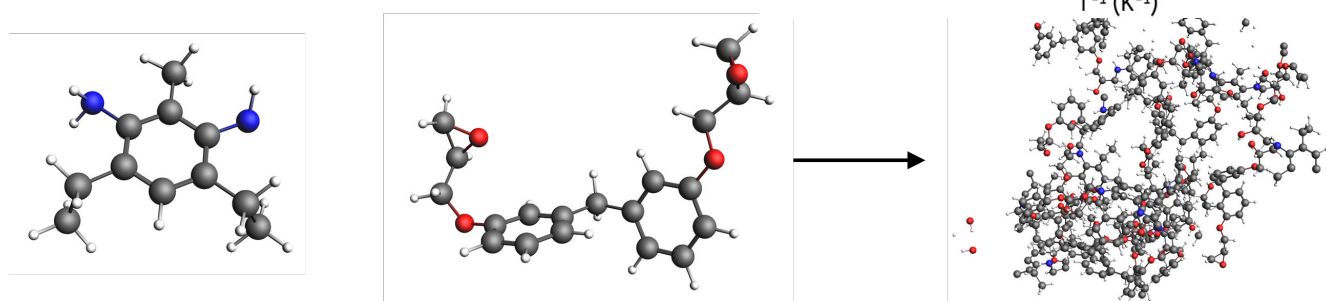
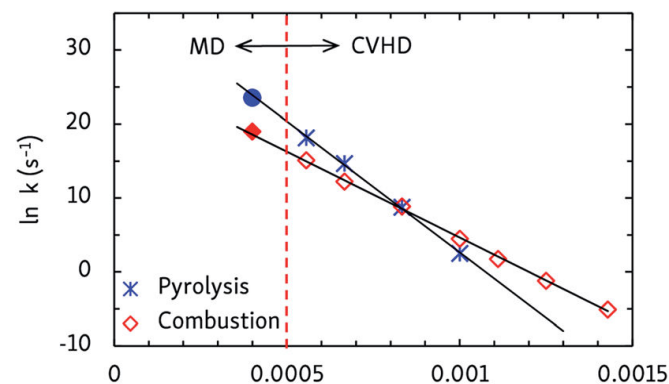
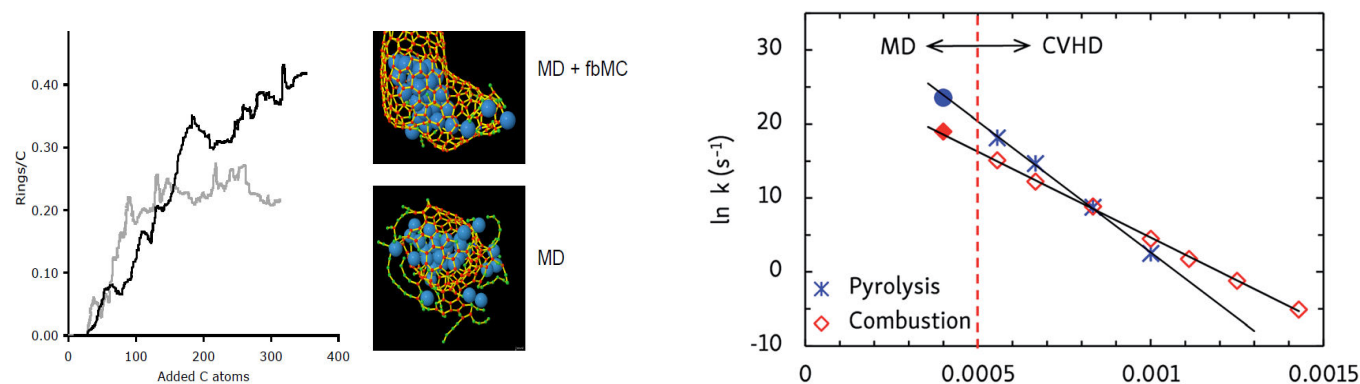
Tools += complete reaction networks  
 elementary reactions, rate constants, fluxes, timeline

[Molecule gun](#): depositing molecules on surfaces

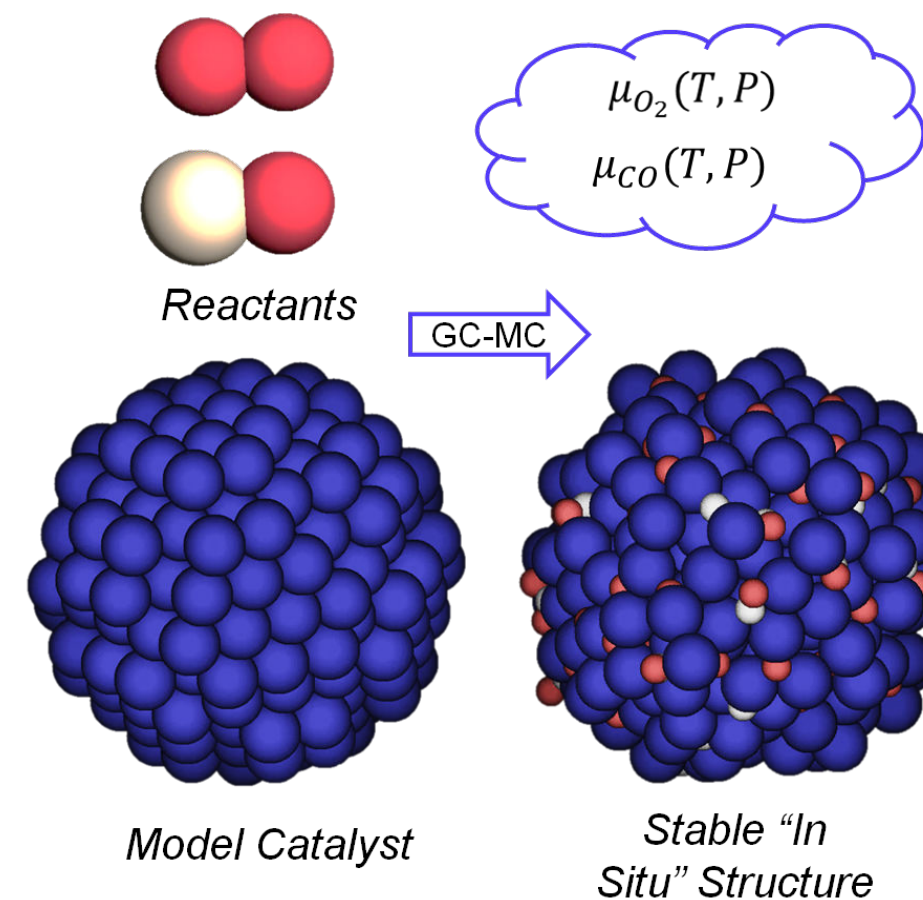


[MCFF & CMA-ES](#) parameterize ReaxFF force field

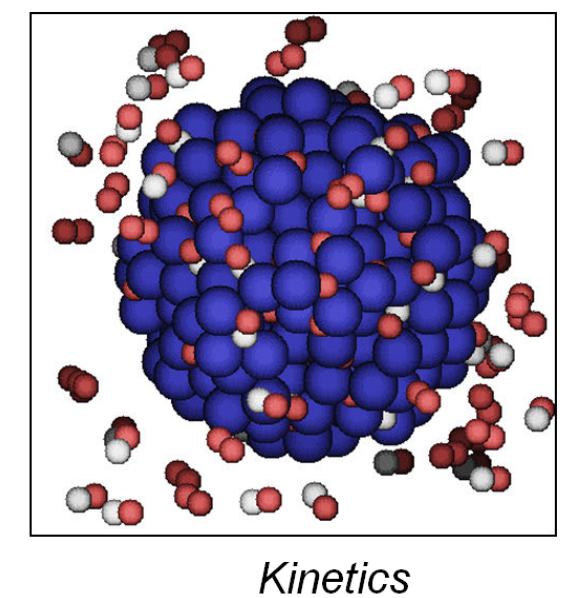
[fbMC](#), CVHD: speed up kinetics



[bond boost](#)  
 build polymers



[GCMC](#): speed up thermo



# ReaxFF: some tips

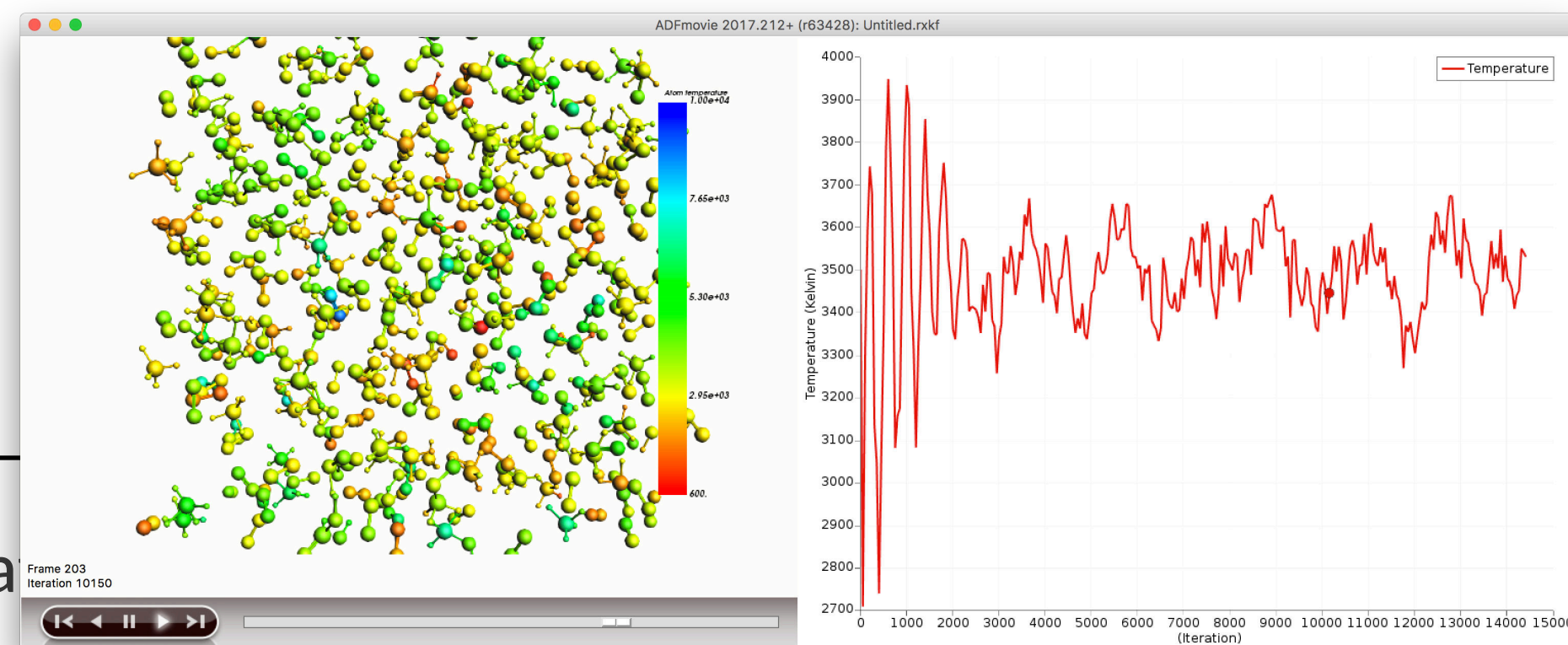
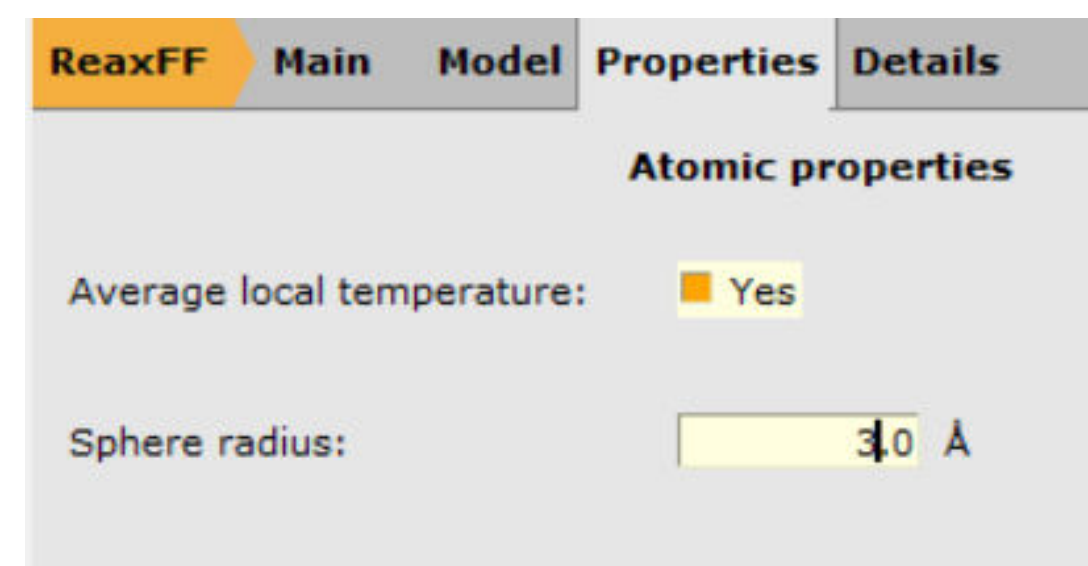
- First equilibrate your system before your production run
  - Usually thermostats equilibrate within some dozen ps, barostats take longer
  - For your equilibration, save less frames (Output frequency in Details-> MD)
  - If equilibrated, restart (Details->Restart) or just copy-paste last geometry
  - Check if your system properly equilibrates => damping constants
    - For Berendsen barostat, use a high damping (e.g. 2500fs), thermostat ~100 fs is OK
    - For NHC thermo/barostat check oscillation and adapt tau (see also [manual](#))
- After importing a structure (cif, database, ..): relax the system
  - Geometry optimization with loose criteria
  - OR run a few ps NpT trajectory with a 0.05fs time step at 5K and 0 pressure
- Avoid having lattice vectors < 10 Å
- See our [FAQs, e.g on ReaxFF force field availability / suitability](#)
- Contact [support@scm.com](mailto:support@scm.com)



# ReaxFF new: local T

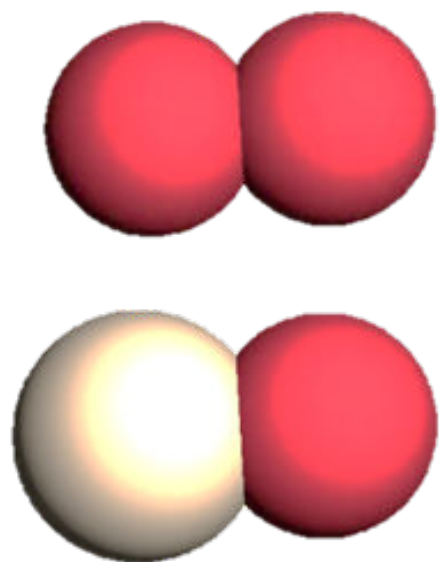
## Try yourself: seeing local temperature variations

- Start with the [methane burning tutorial](#) (or with the [molecule gun](#); see also [news item](#) with tutorial on visualizing local T)
  - Also local documentation! (Search in GUI)
  - Perhaps reduce the # of steps
- To visualize local temperatures:
  - Properties -> Atomic Properties
  - Tick Average local temperature
  - Set the awareness radius to 3.0 Å
- Local T in ADMovie: view -> color atoms by -> Local T
  - Change the axes and the color coding after double-clicking the legend
  - Also do the ChemTraYzer analysis

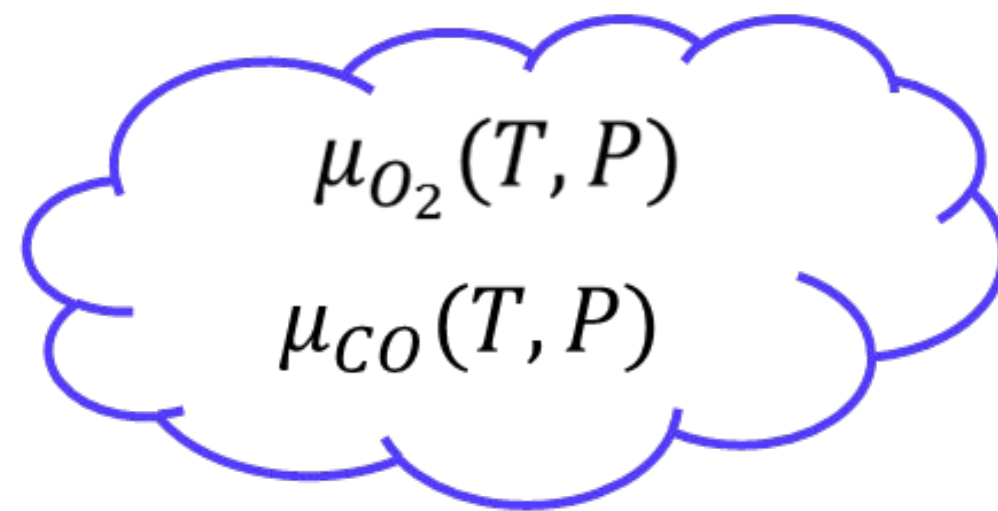




# Grand Canonical Monte Carlo + ReaxFF



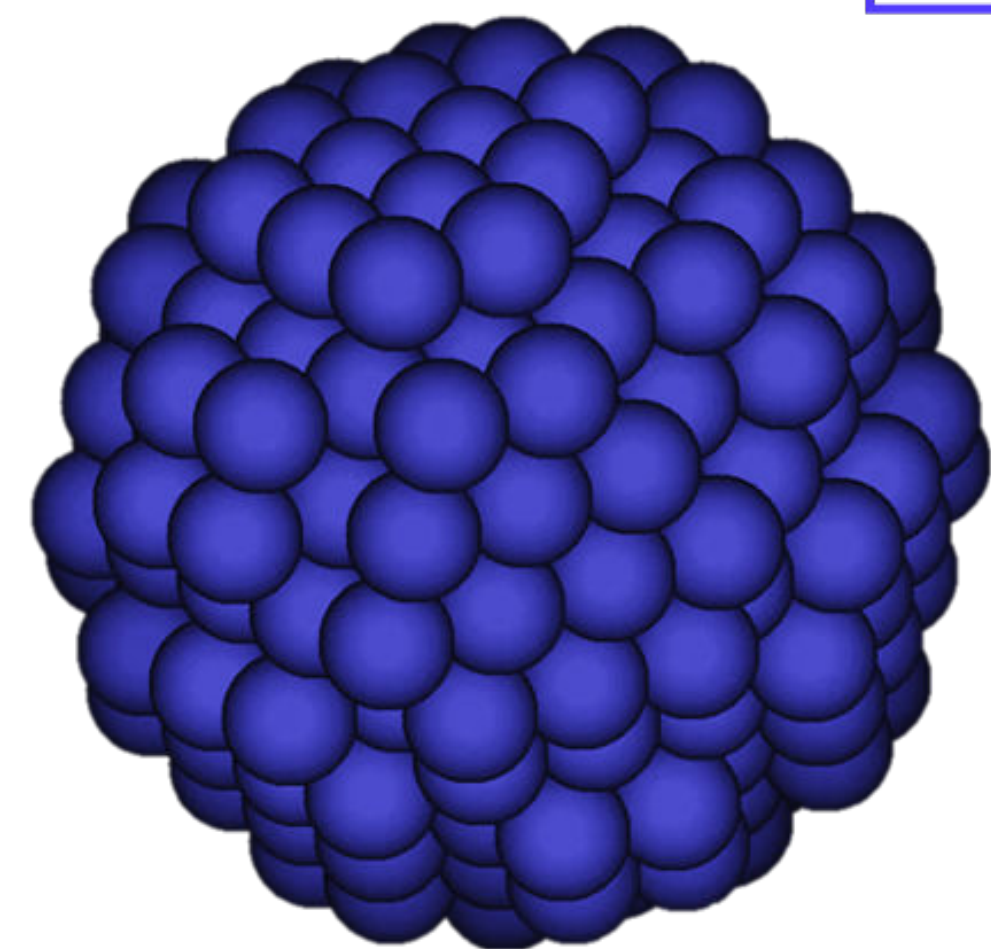
Reactants



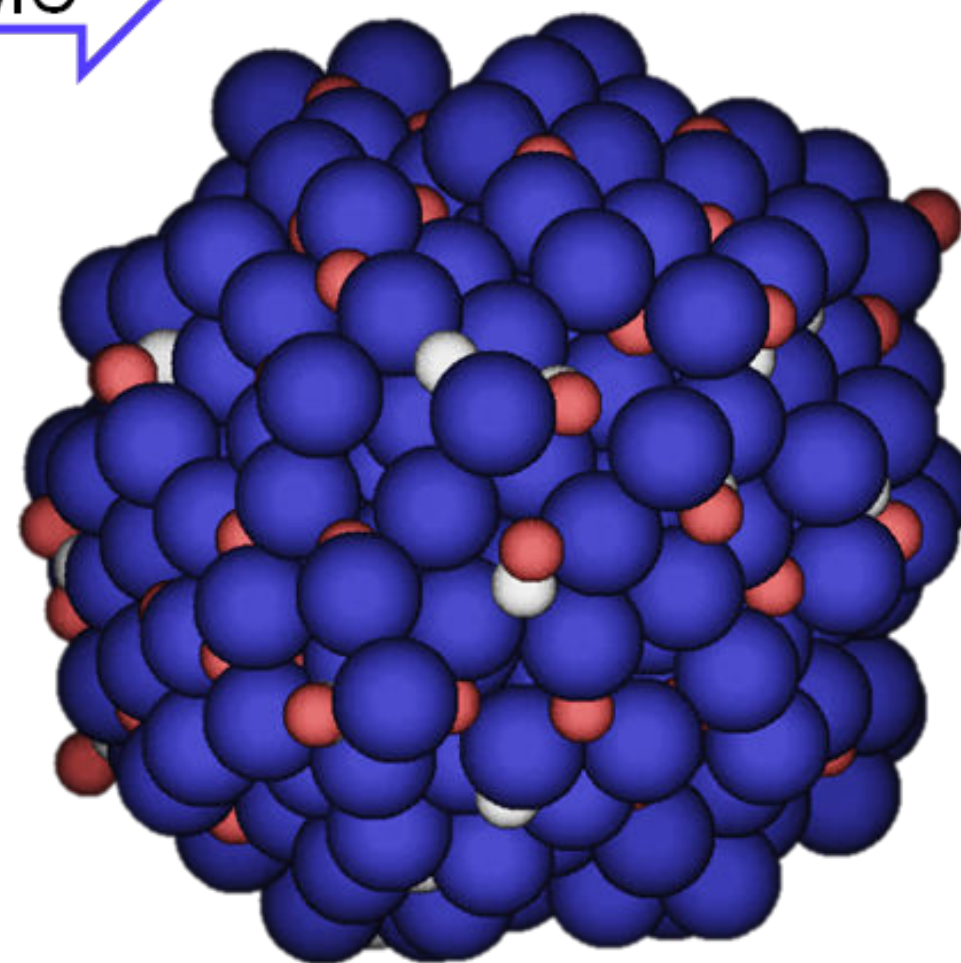
Reactive MD under actual conditions

GCMC: What is stable (p,T)?

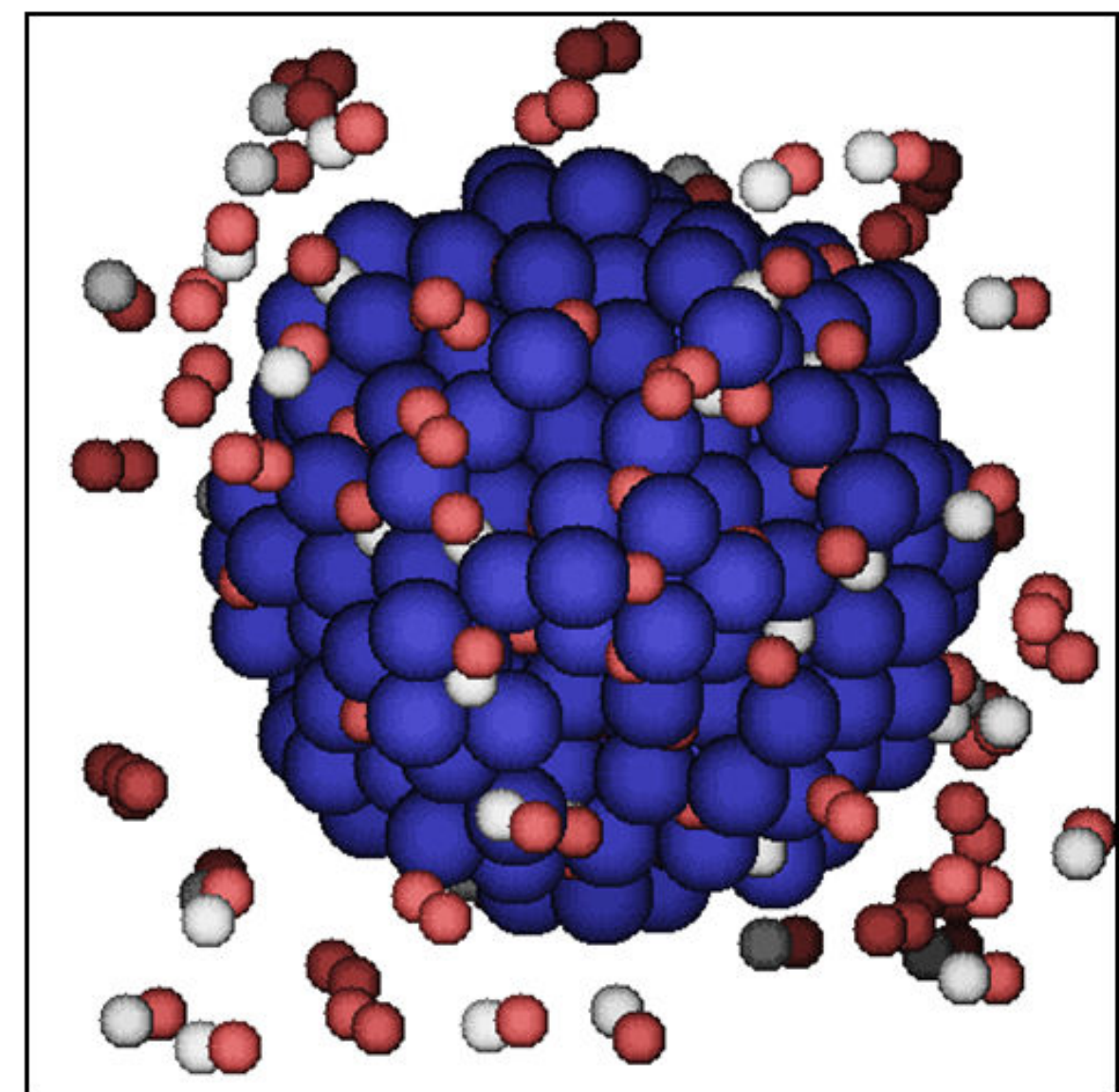
ReaxFF: What is active?



Model Catalyst



Stable "In Situ" Structure



Kinetics

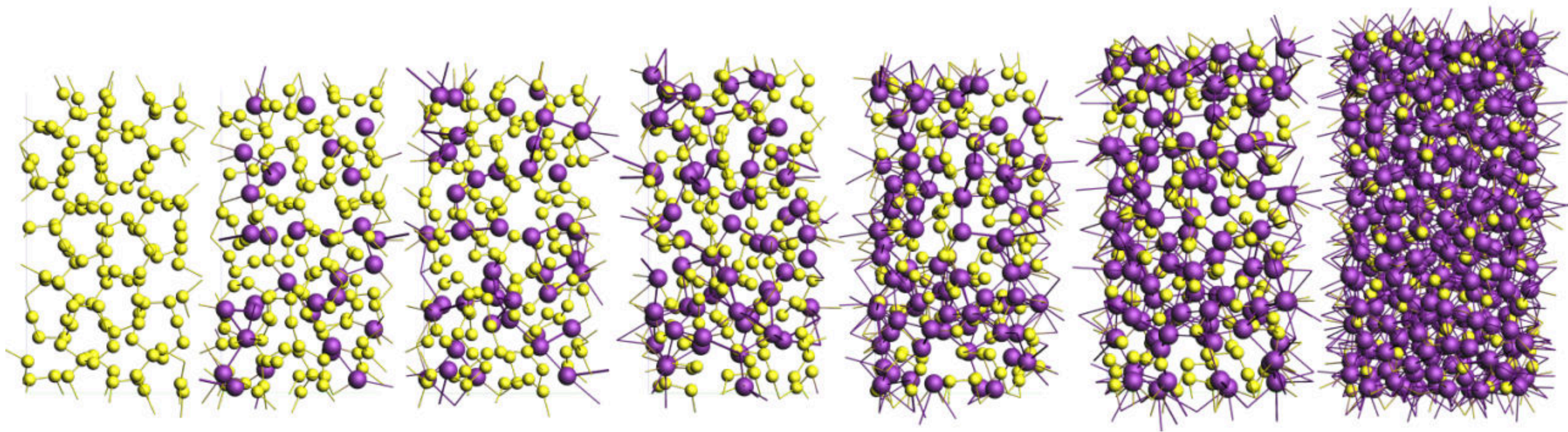
[ReaxFF + GCMC tutorial](#)

T.P. Senftle, R.J. Meyer, M.J. Janik, A.C.T. van Duin, J. Chem. Phys., 139 (2013) 044109



# ReaxFF: GCMC battery voltages

Try yourself: [advanced GCMC battery discharge tutorial](#) inserting Li in S



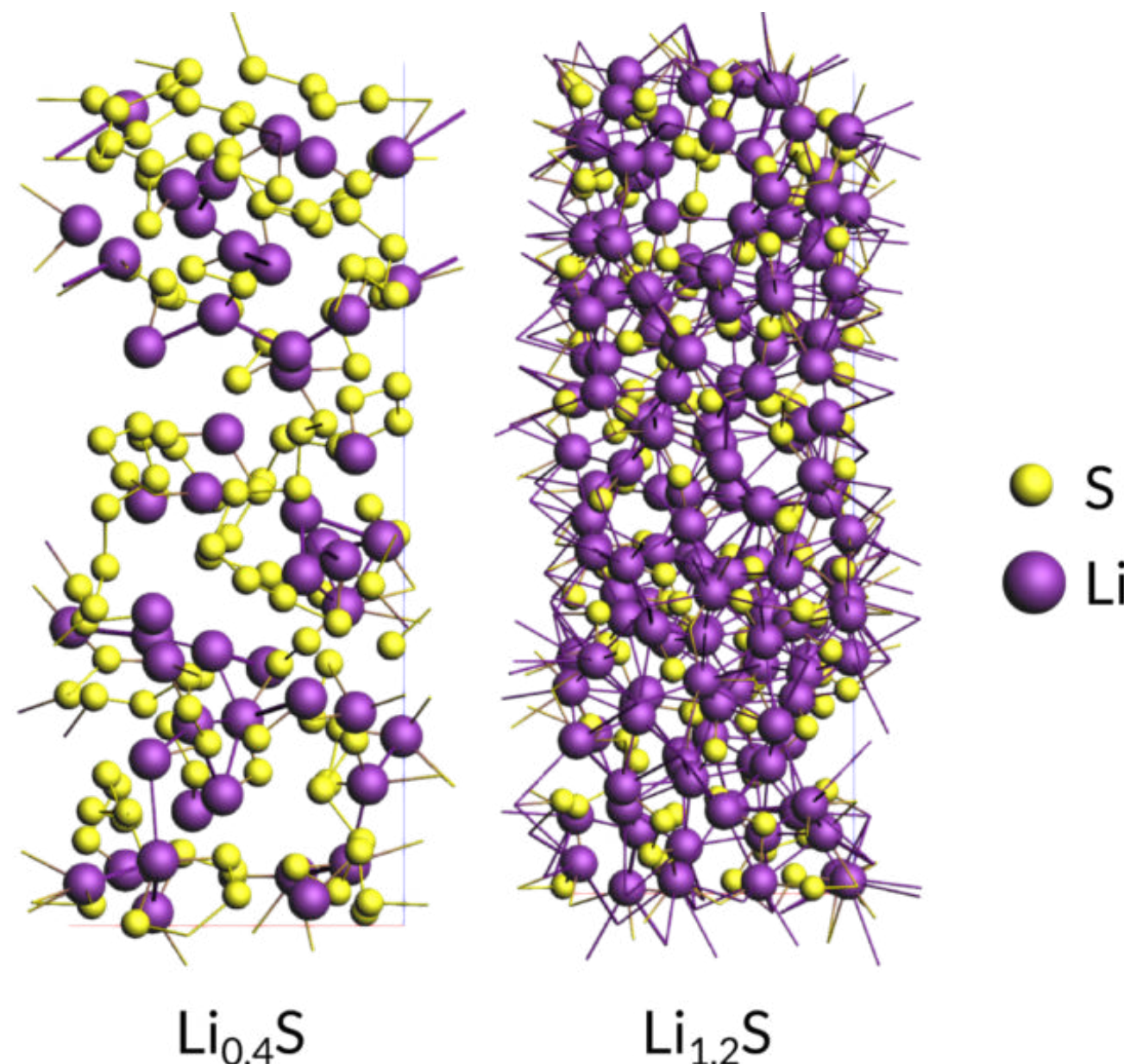
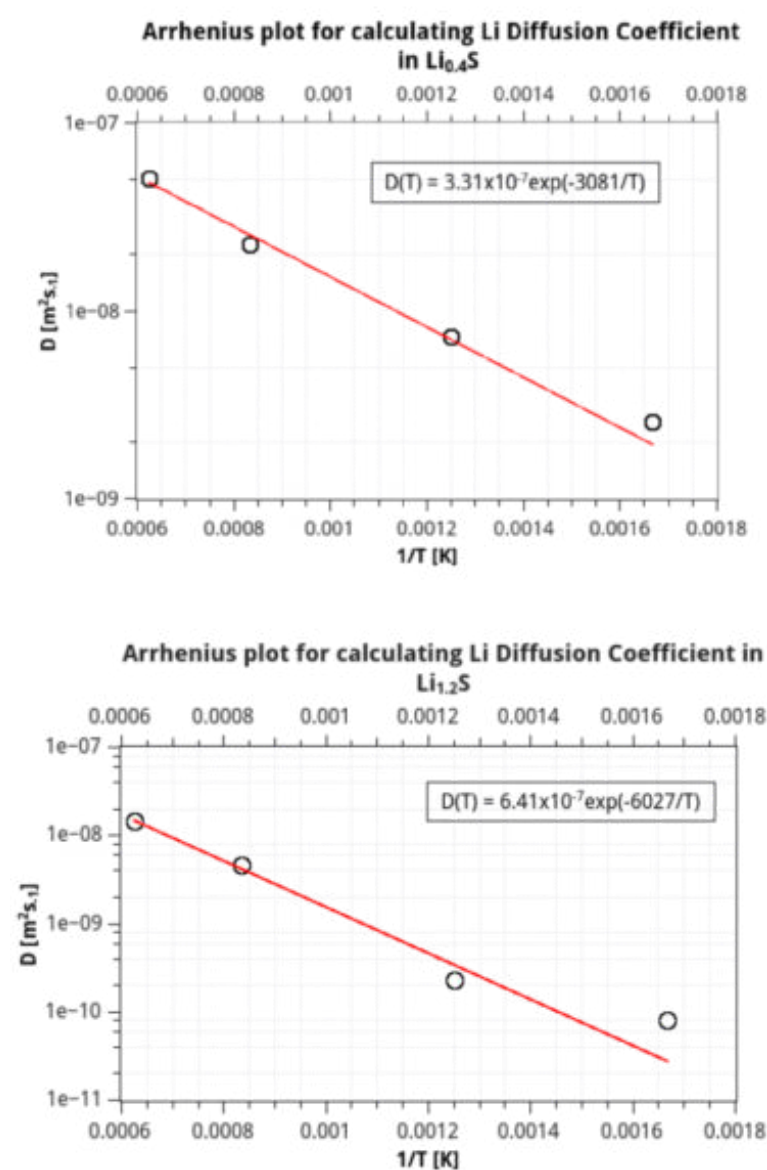
Based on: M. M. Islam, A. Ostadhossein, O. Borodin, A. T. Yeates, W. W. Tipton, R. G. Hennig, N. Kumar, and A. C. T. van Duin, *ReaxFF molecular dynamics simulations on lithiated sulfur cathode materials*, [Phys. Chem. Chem. Phys. 17, 3383-3393 \(2015\)](#)



# ReaxFF: Li diffusion in batteries

Try yourself: [advanced tutorial Li diffusion](#) (same  $S_8$  coords as GCMC)

- A more robust way to make the  $Li_{1.2}S$  system (step In step 2.2):
  - Take the optimized  $Li_{0.4}S$  system, change the lattice c-vector to 38 while ticking 'Adjust atoms'
  - Delete all Li atoms (select one, then select atoms of some type)
  - Now use Packmol ('Builder) to add 154 Li atoms... & do a longer NpT run (!5000 steps? – check Energy)
  - Or even better: take one of the GCMC structures from Exercise 15
  - To properly anneal – a slow cooling rate is recommended (rather than the fast one used here)
  - Check p, T and E during NpT equilibration – stop when it looks 'flat' and 'Update Geometry'



**Travis is a bit difficult to use:**

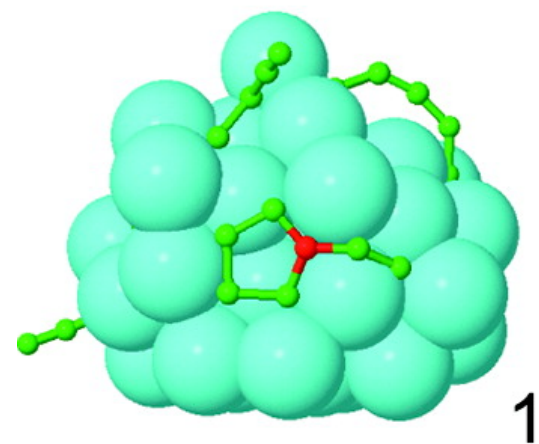
We will develop native analysis tools

You can also write script in PLAMS

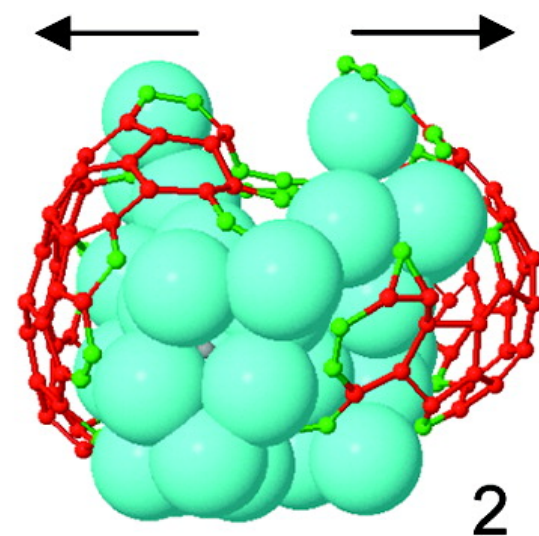


# Carbon nanotube formation: accelerate MD

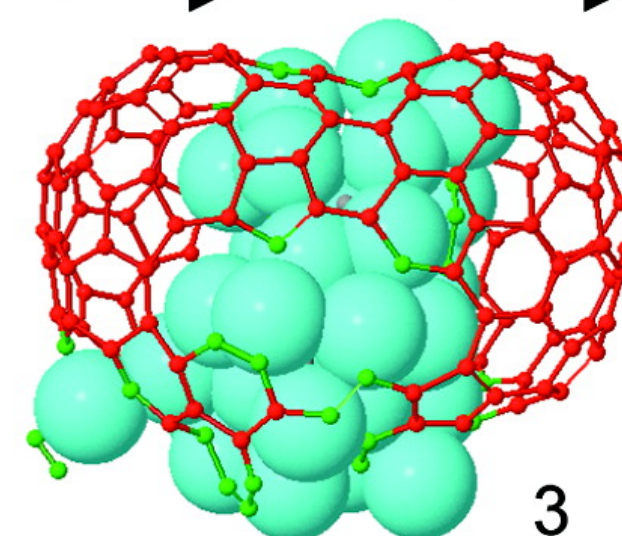
pentagon formation



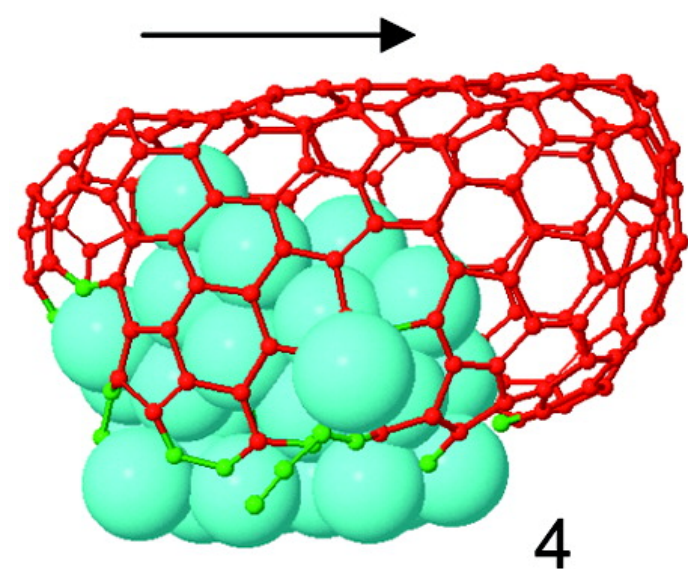
graphitic patches



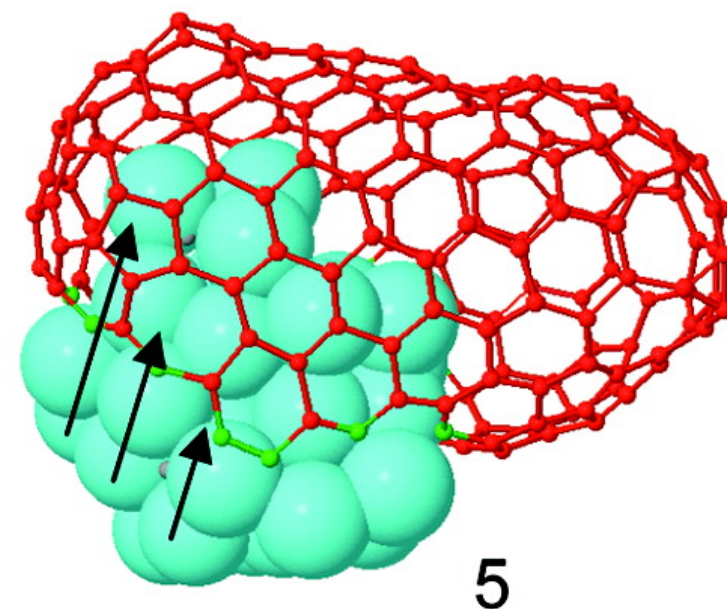
cap development



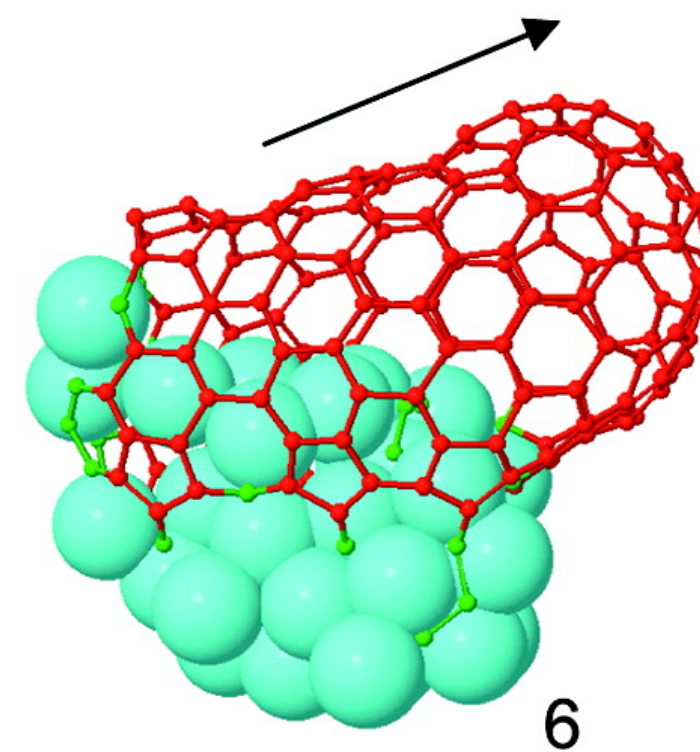
carbon network slides over catalyst



part of metal gets freed



end of sliding, chirality obtained



Try:  
[fbMC tutorial](#)  
[graphene healing](#)

ReaxFF-MD + fbMC: healing of defects during sliding of network (steps 4-5).  
First simulation showing growth of an armchair SWNT with **definite chirality** on catalyst.

[Molecule gun + fbMC video](#)

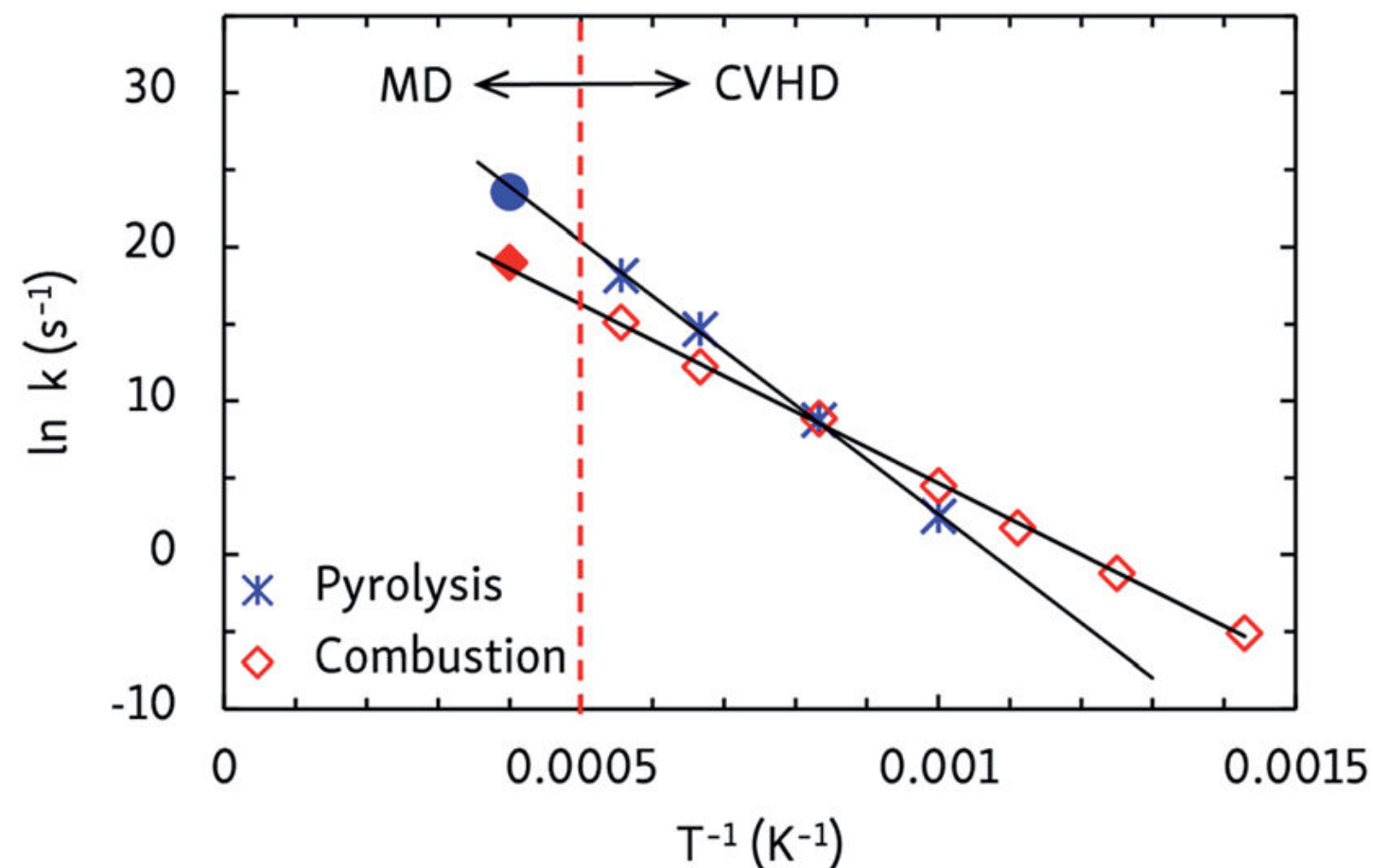
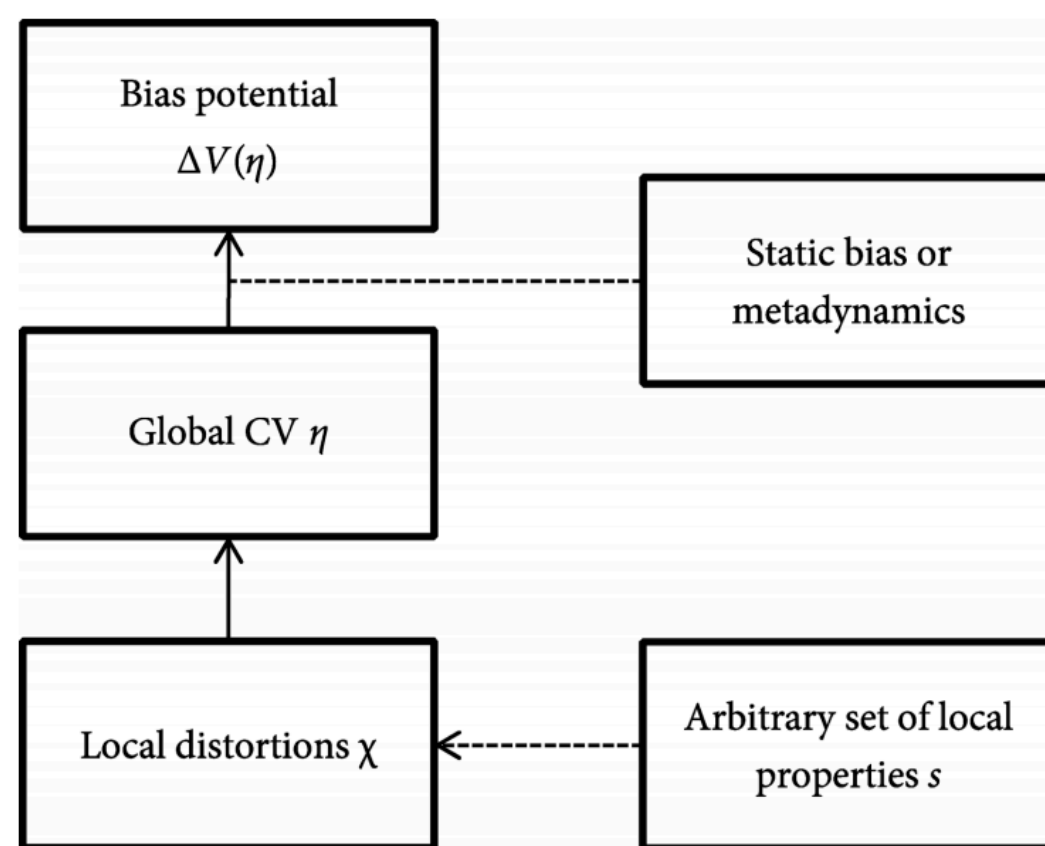
Neyts *et al.*, *J. Am. Chem. Soc.* **133**, 17225 (2011)



# Further accelerating ReaxFF

## Collective-Variable driven Hyperdynamics (CVHD)

- Metadynamics meets hyperdynamics; learn CV 'on-the-fly'
- Boosts:  $10^6 - 10^9$  for pyrolysis / combustion

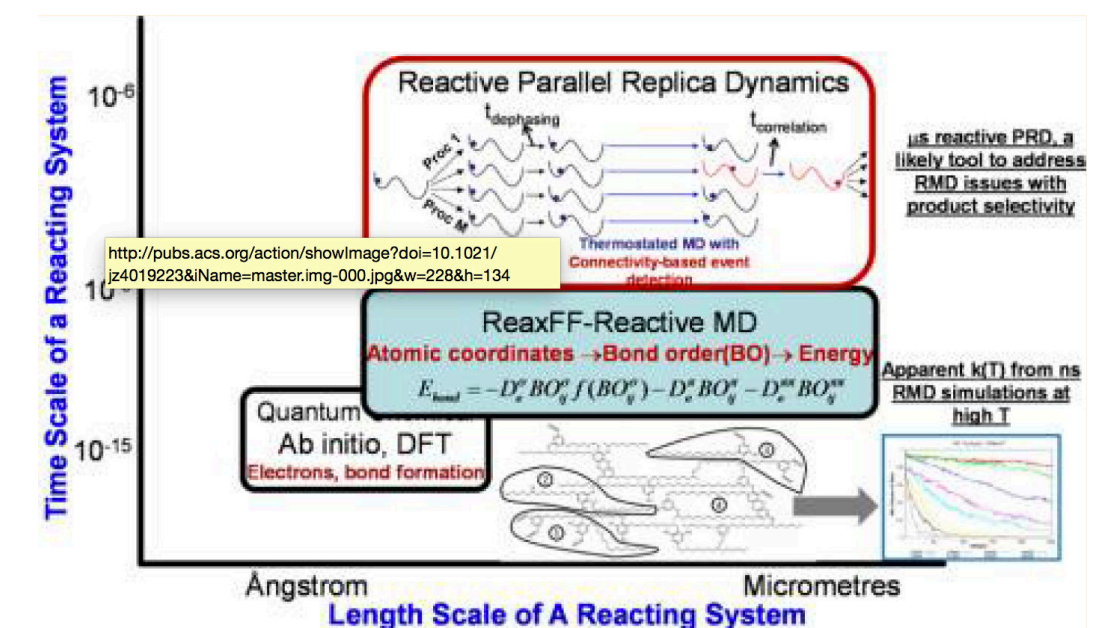


[Try: tutorial](#)

Bal & Neyts: [J. Chem. Theory Comput. 11, 4545 \(2015\)](#); [Chem. Sci., 7, 5280 \(2016\)](#)

## Under development:

- Multi-replica methods (T-REMD, PRD)
  - Easy set-up, no bias (NB: PRD needs pre-defined event)
- (Path sampling approaches: TPS, TIS, ....)

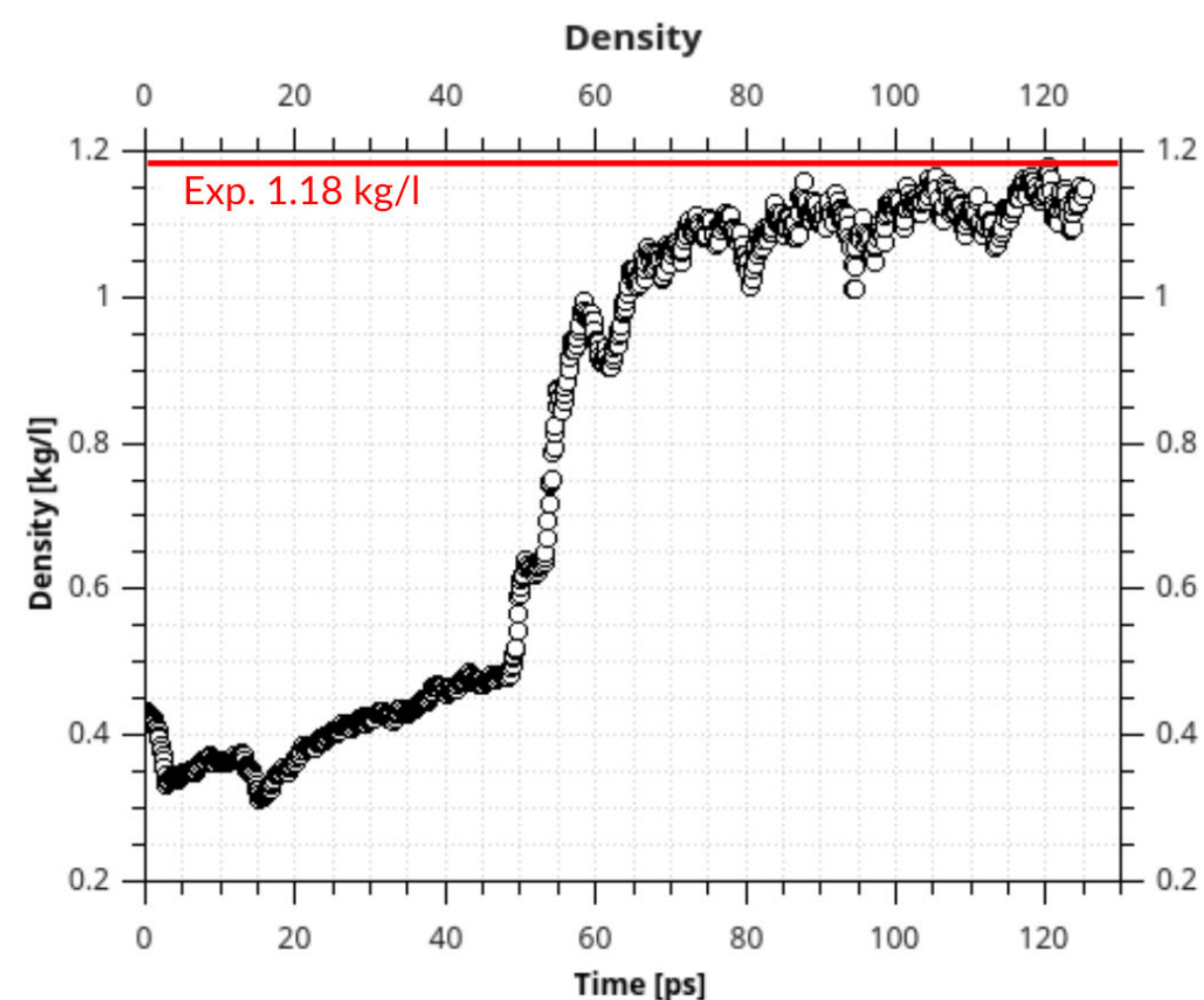
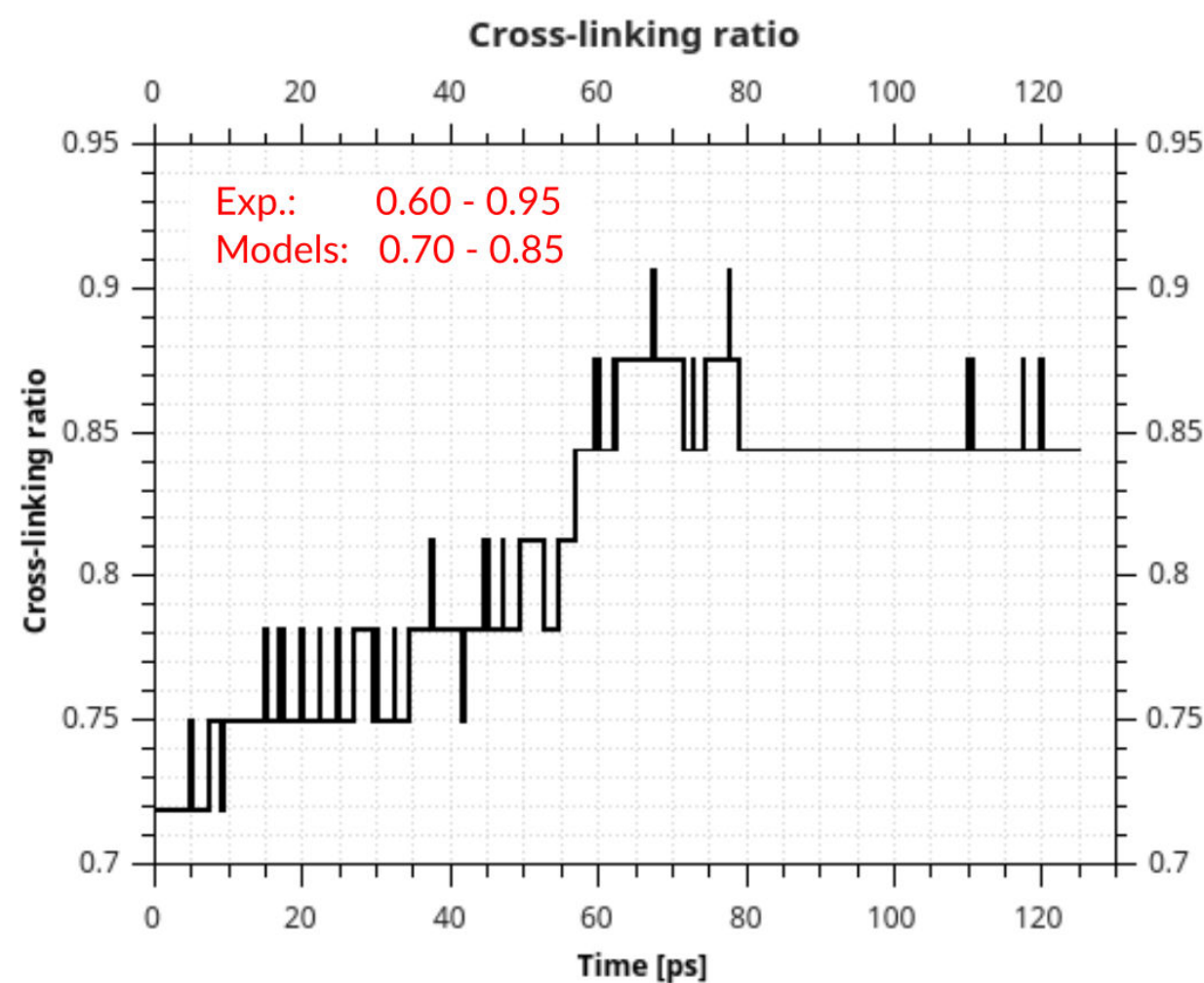
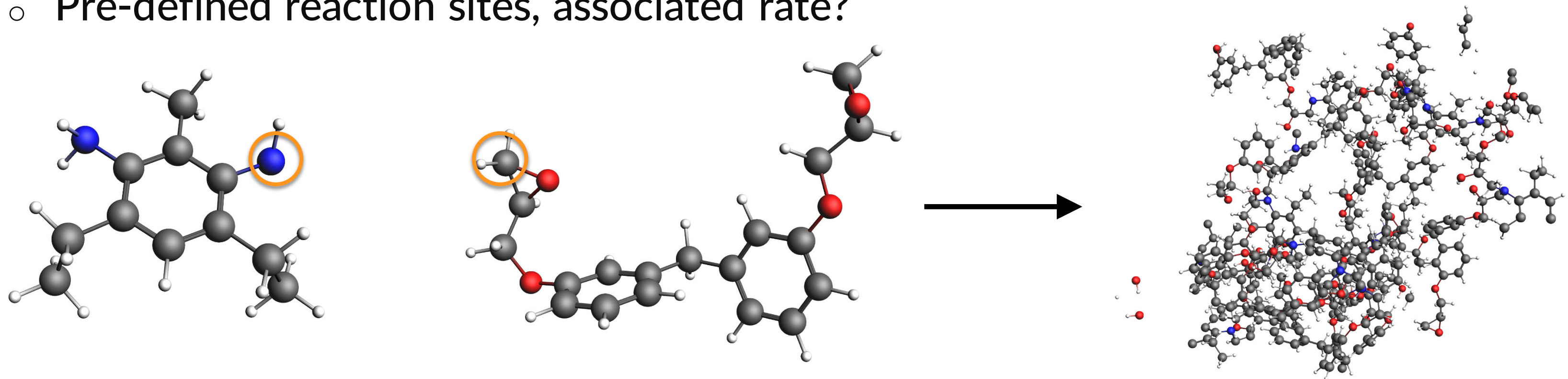


J. Phys. Chem. Lett. 4, 3792 (2013)



# Further accelerating ReaxFF

- 'Bond boost' (van Duin)
  - Cross-link polymers (irreversible) – can be extended to other reactions
  - Pre-defined reaction sites, associated rate?

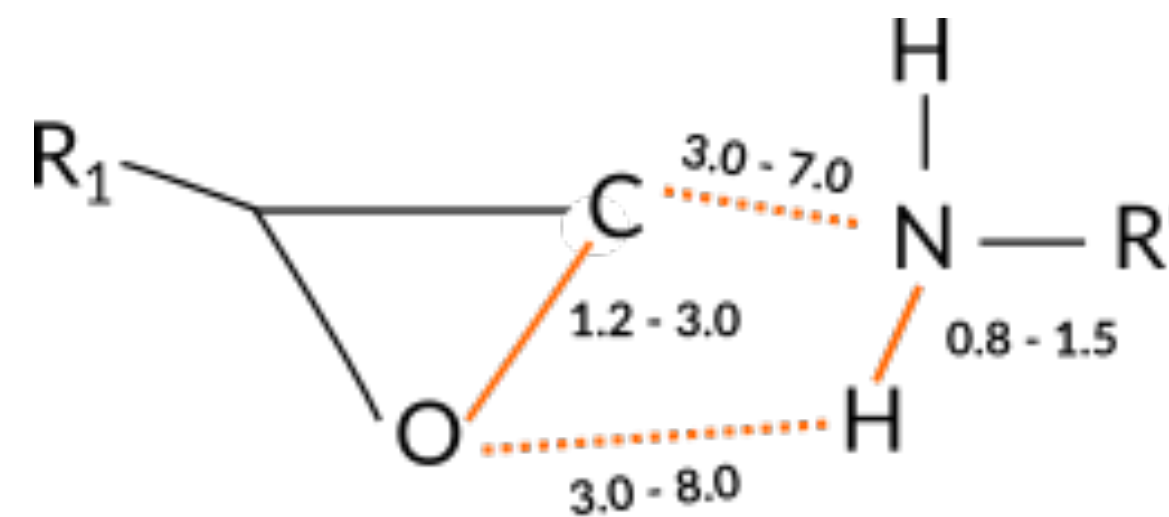




# ReaxFF: bond boost

Try yourself: [start with bond boost tutorial](#) (part is used in ReaxFF training set)

- Add boost potential when reactions are 'close to reaction', but not over barrier!
- Track bond distances of certain atoms =>
  - Needs tweaking for new ff or rxn => new param
- For small systems: easy to set up in GUI
- For bigger systems use **python scripting**
  
- Also check out [mechanical polymer properties](#)



preliminary complex

[van Duin et al., J. Phys. Chem. A \(2018\)](#)

ReaxFF Main Model Properties Details

Bond Boost

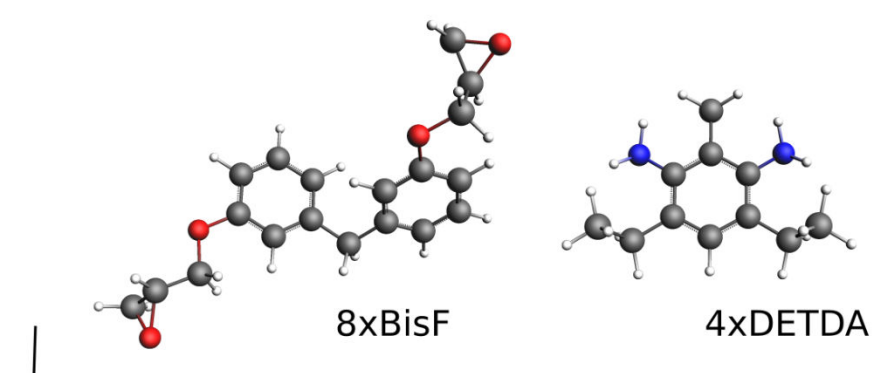
Boost lifetime: 10000 iterations

+ Detect initial configuration

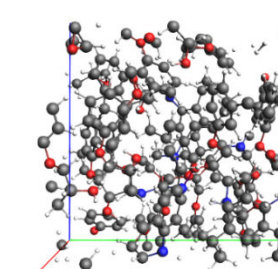
Atom types (names and regions)		Rmin, Rmax Å
1: N-AllN	2: C-CT	3.0 7.0
2: C-CT	3: O-AllO	1.2 3.0
3: O-AllO	4: H-AllH	3.0 8.0
4: H-AllH	5: N-AllN	0.8 1.5

+ Add boost

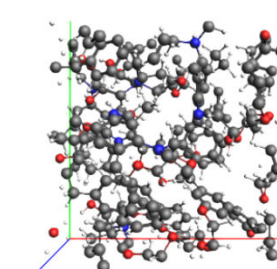
Atom1	Atom2	R <sub>0</sub> Å	F <sub>1</sub> kcal/mol	F <sub>2</sub> Å <sup>-2</sup>
1: N	2: C	1.5	400.0	0.75
3: O	4: H	1.5	300.0	0.5
2: C	3: O	2.5	100.0	0.75



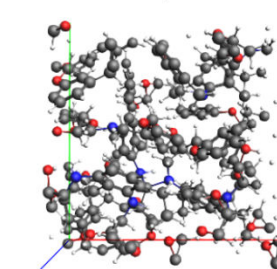
bond-boost.py ~ 1h per structure (on 4-cores)



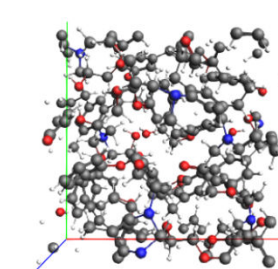
#1  
X-link ratio = 0.81



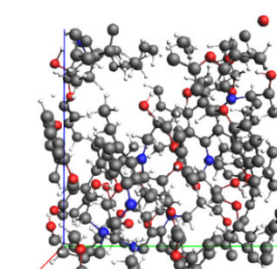
#2  
X-link ratio = 0.69



#3  
X-link ratio = 0.63



#4  
X-link ratio = 0.88

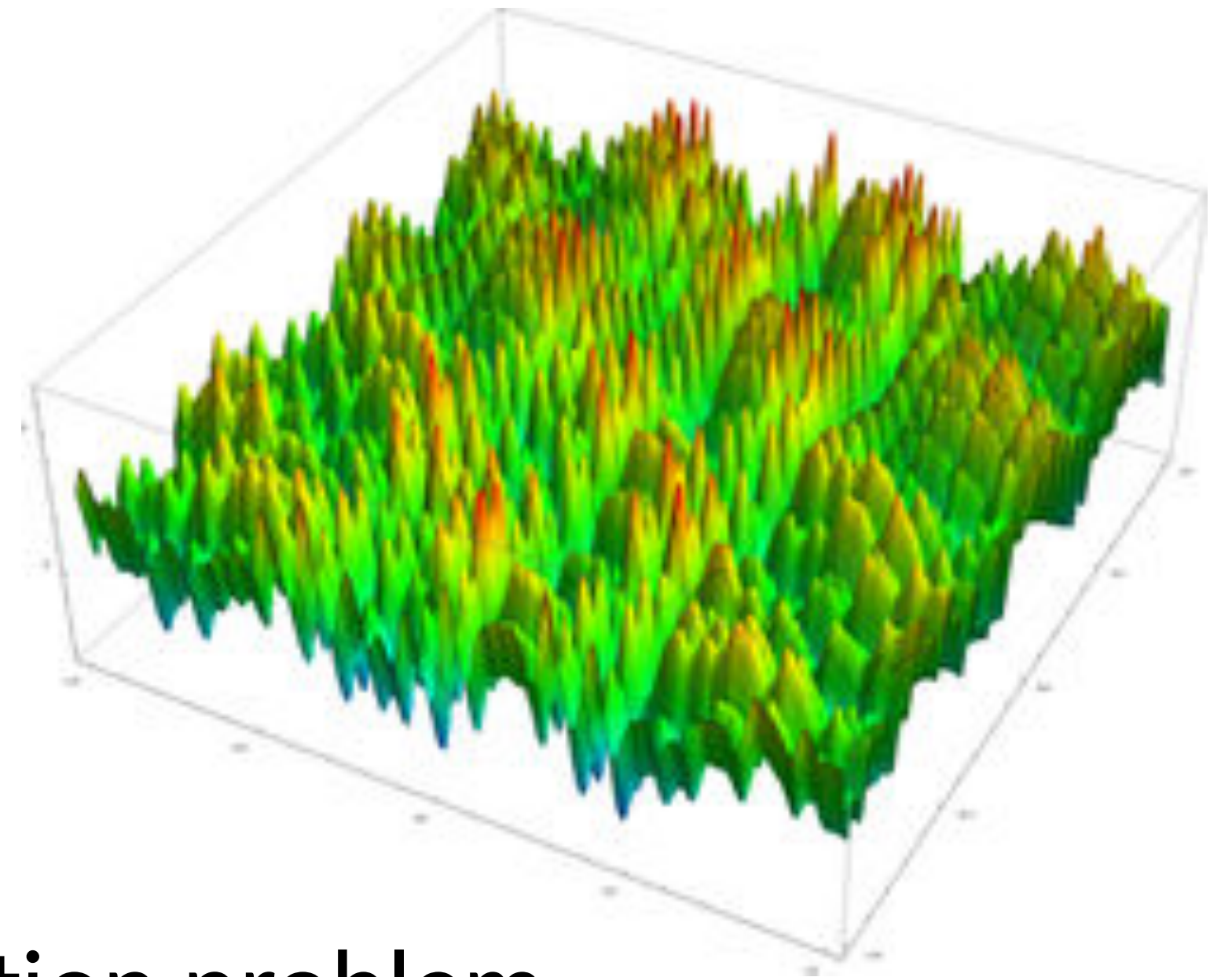


#5  
X-link ratio = 0.81



# Optimizing ReaxFF parameters

- Parameters are
  - interdependent
  - non-linear
  - many
  - not always physically interpretable
- Highly complex global optimization problem





# Monte Carlo with Simulated Annealing

$$Error = \sum_{i=1}^n \left[ \frac{(X_{i,TS} - X_{i,ReaxFF})}{\sigma_i} \right]^2$$

$X_{i,TS}$  = reference

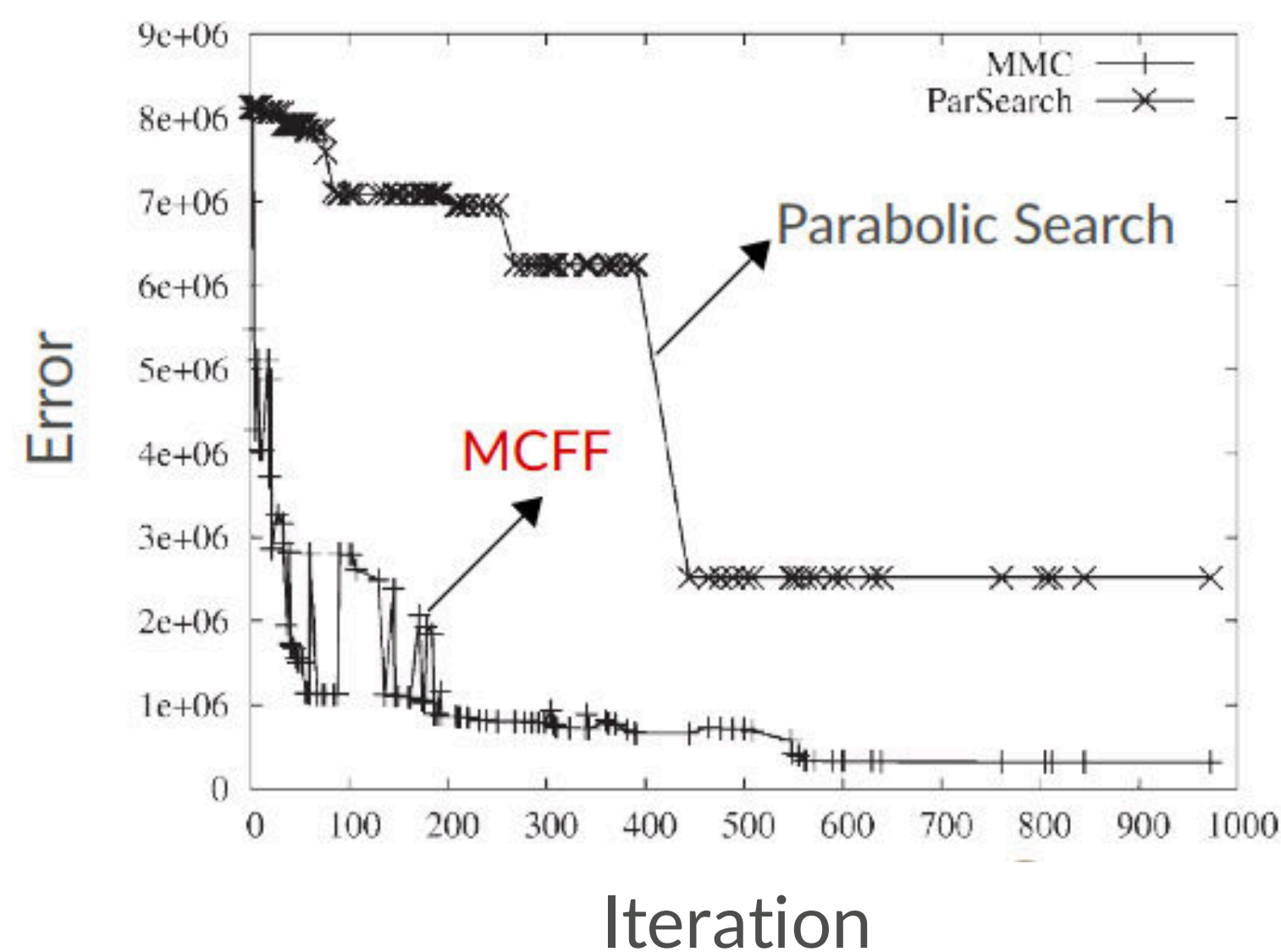
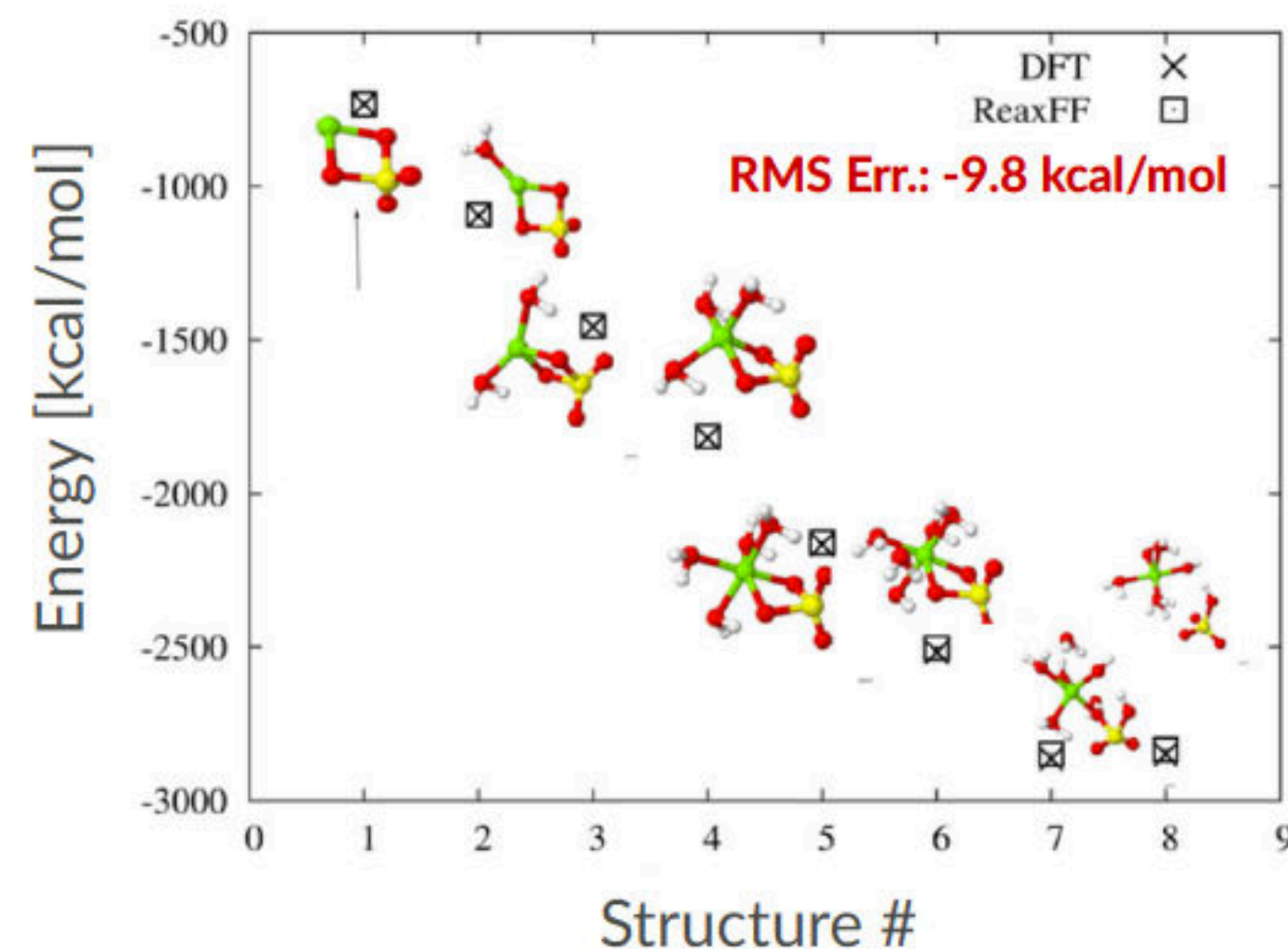
$X_{i,ReaxFF}$  = current ReaxFF

$\sigma_i$  = weight

References include:

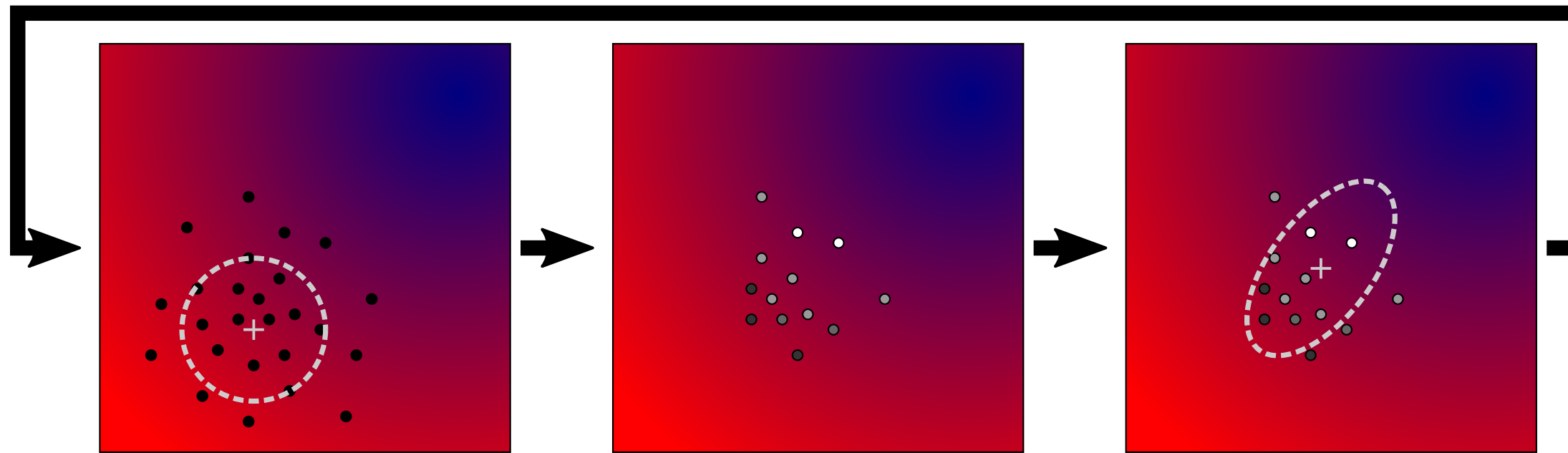
- Atomic charges
- Heat of formation
- Geometries (Bond/Angle/Dihedrals)
- Cell parameters
- Energies

[J. Comp. Chem. 34, 1143-1154 \(2013\)](#)





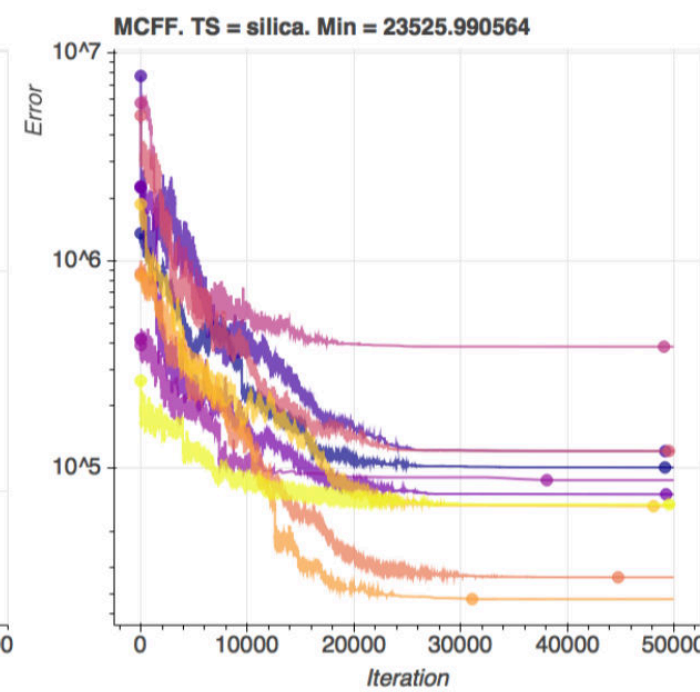
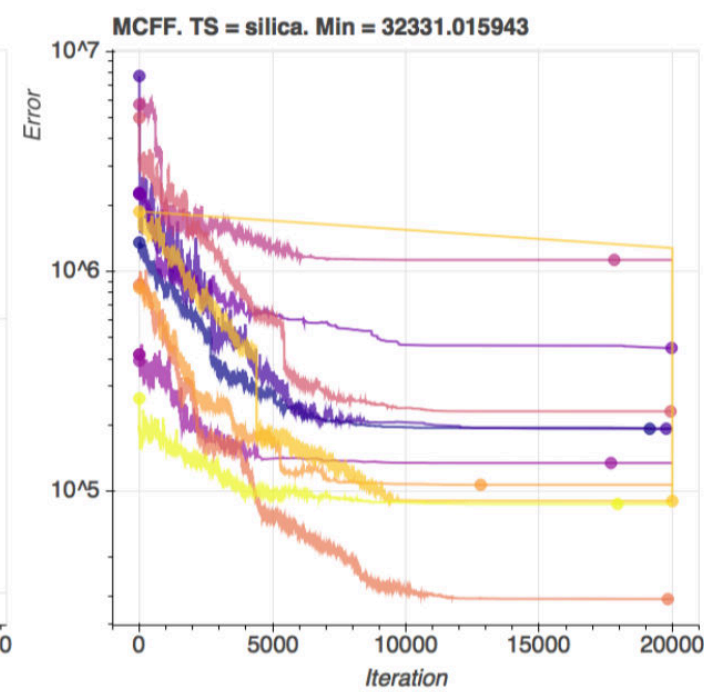
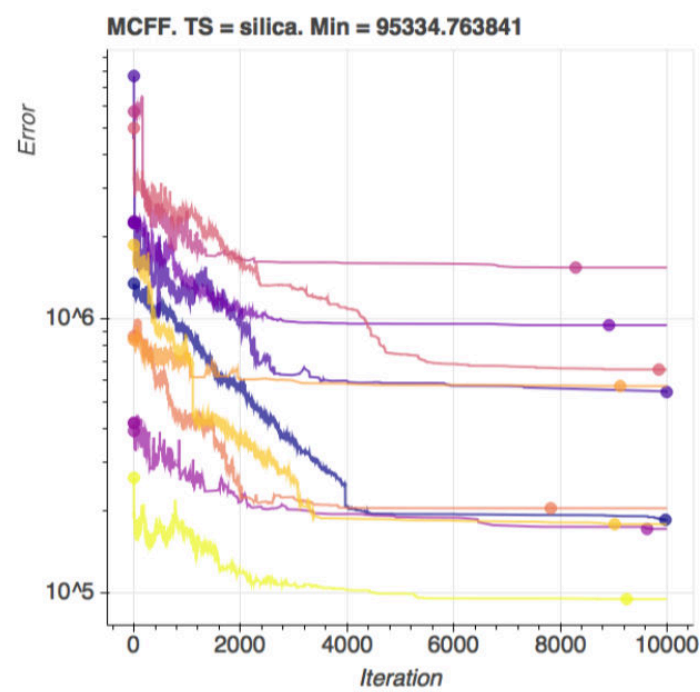
# Covariance Matrix Adaptation Evolutionary Strategy



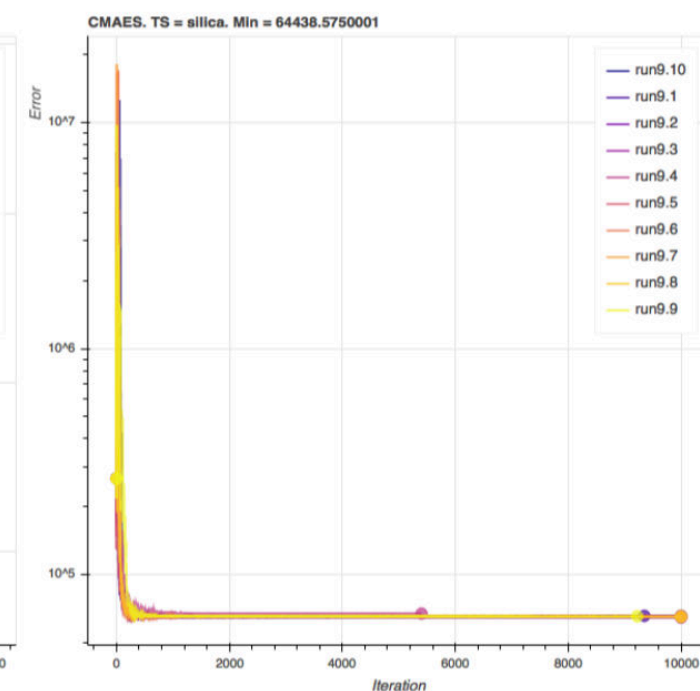
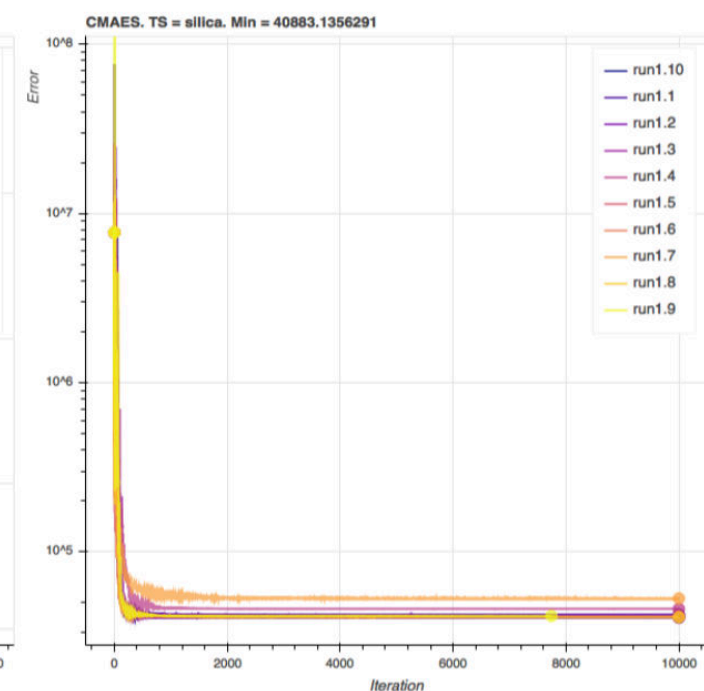
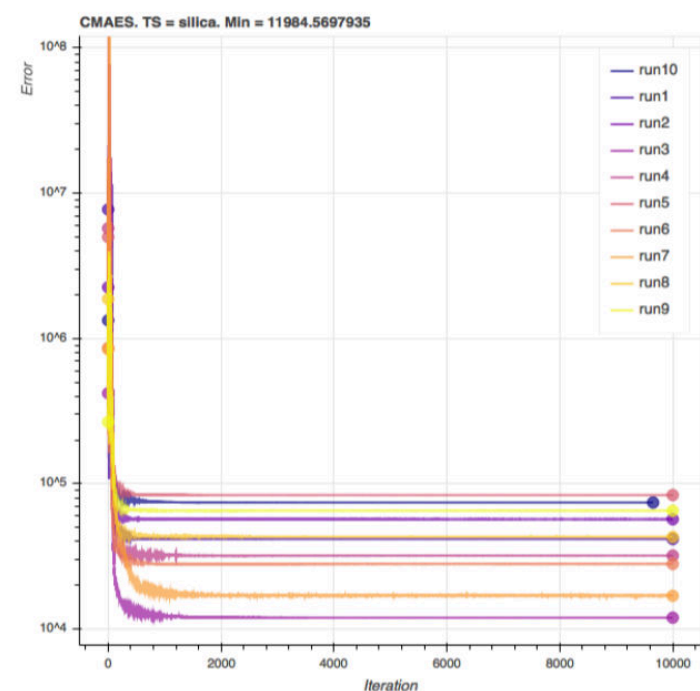
Generate points using multivariate Gaussian distribution with covariance matrix  $C$

Order the points by their objective function value  
Assign weights, decreasing from the best point to the median

Set new distribution center to weighted average of successful points  
Update covariance matrix



## MCFF



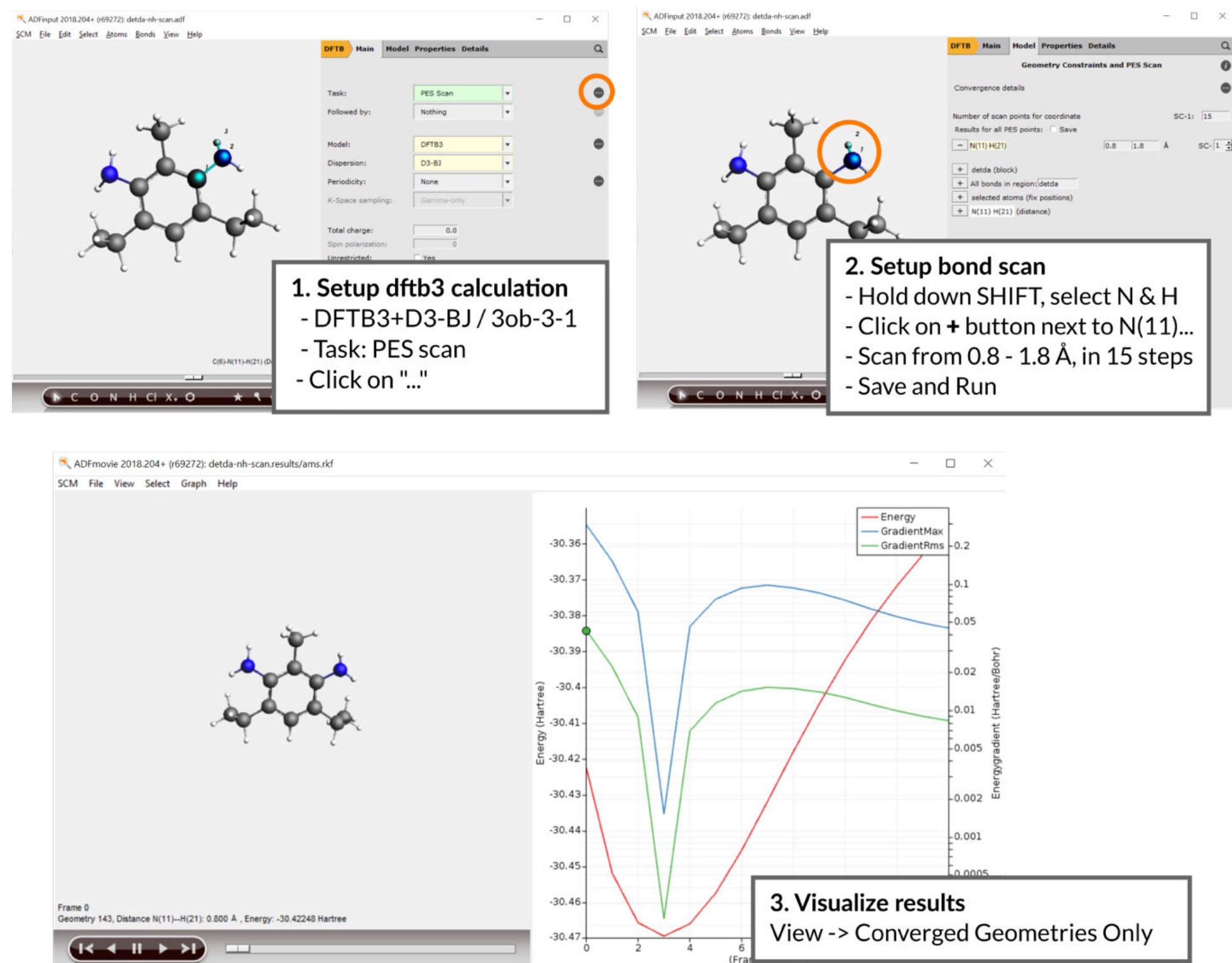
## CMA-ES (Shchygol et al. arxiv)



# ReaxFF: reparameterization

## Refine ReaxFF parameters for cross-linking polymers

- Follow the tutorial package to build your training set (trainset.in & geo)
  - Take care with adding the geometries into one file and editing the trainset
  - A lot of work, some scripting
- Add geometries
- Add conformers, trajectories
- Add bond scans
- Run CMA-ES optimization
  - Try different #, length, width, ...
- Test errors, cross-validate
- Try to further refine

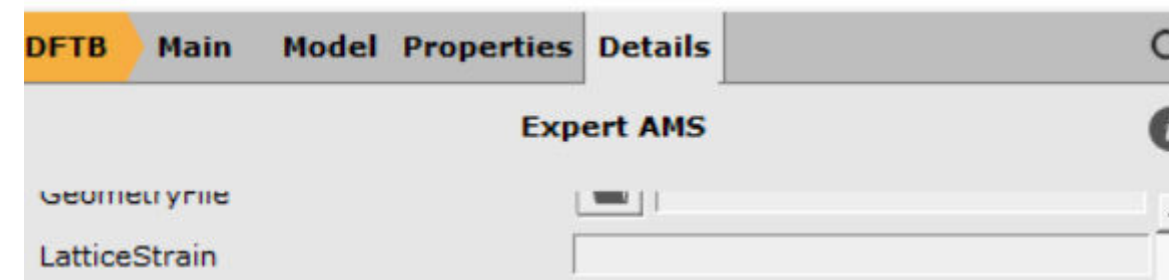
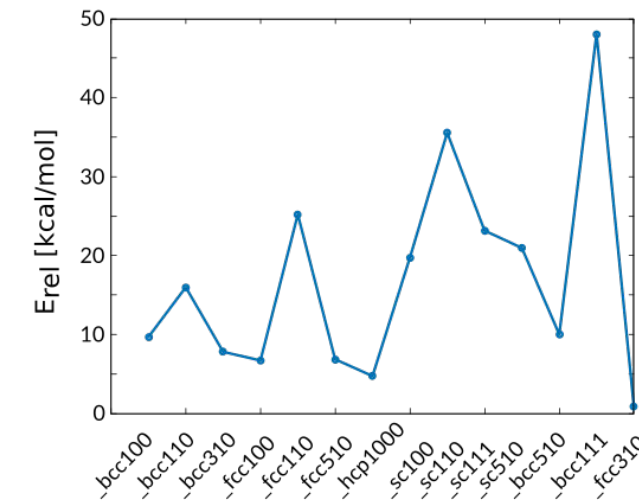
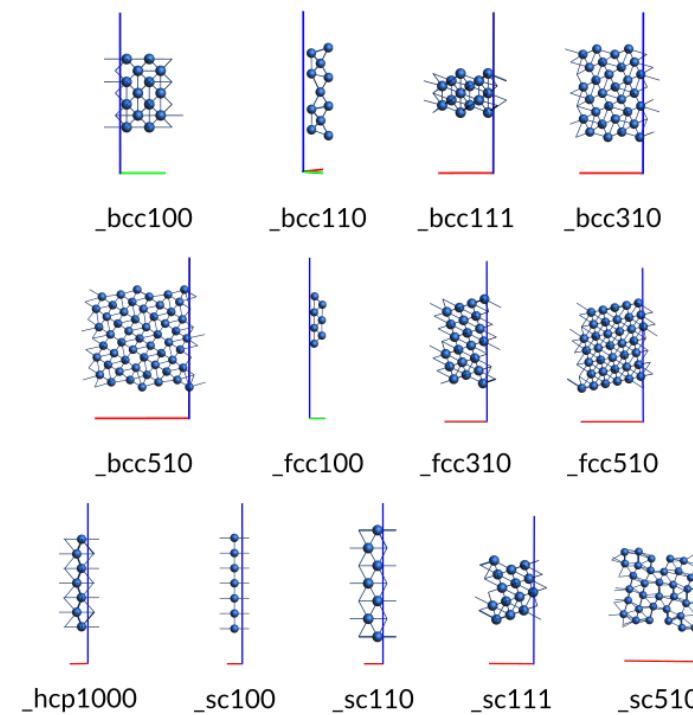




# ReaxFF parameterization alloys?

- See also: [Co training set](#)

- Relative crystal energies
- Equation of State, elastic tensor
- Cohesive energy
- Defect, adsorption energy
- Surface energies
- conformers2trainset works with E vs V
  - Stretch e.g. a,b,c
- GUI: use lattice strain (Expert AMS)
- More tools underway (on ReaxFF fitting webpage)

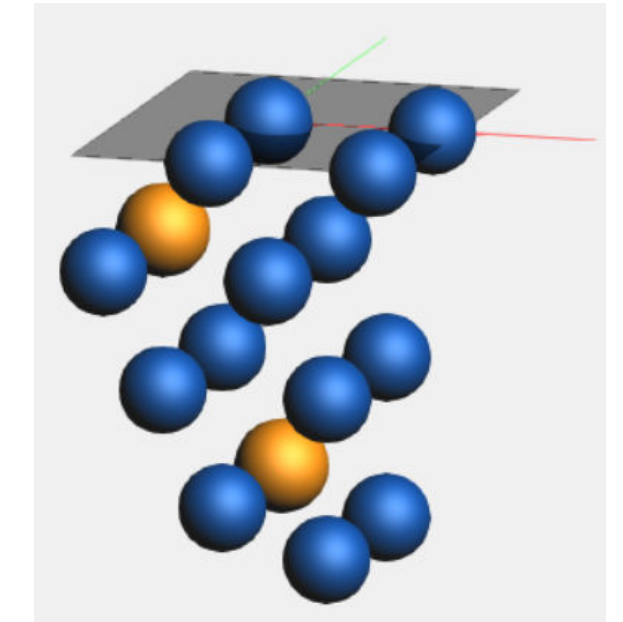
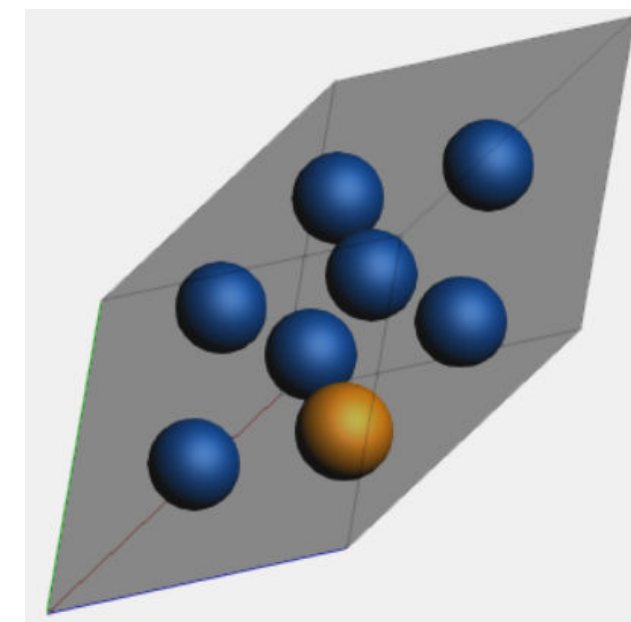


- Adding mixing energies (e.g. add Rh)?

- $\text{Co}_x\text{Rh}_y$  for bulk, cluster, surface => replace atoms in supercell, e.g.  $1/8$ ,  $1/4$ ,  $1/2$   $H_{\text{form}}$ , EOS
- $\text{Co}_x$  adsorption Rh surface (+ vv)
- Examples from literature:

PtNi : [J. Phys. Chem. A 2016, 120, 8044](#);

Fe/Al/Ni: [J. Phys. Chem. A 2012, 116, 12163](#)





# Some notes on (Windows) scripting

Use help -> command-line and type sh to go to a Windows shell with ADF environment variables set.

```
C:\ADF_DATA\CMA-ES-FIT\xyz>set ADFHOME=C:/ADF2018.105/
C:\ADF_DATA\CMA-ES-FIT\xyz>set ADFHOME_=C:\ADF2018.105\
C:\ADF_DATA\CMA-ES-FIT\xyz>set ADFBIN=C:/ADF2018.105//bin
C:\ADF_DATA\CMA-ES-FIT\xyz>set ADFRESOURCES=C:/ADF2018.105//atomicdata
C:\ADF_DATA\CMA-ES-FIT\xyz>set PATH=C:\ADF2018.105\msys\usr\bin;C:\ADF2018.105\msys\bin;C:\ADF2018.105\bin;C:\ADF2018.105\bin\tcltk\bin;C:\ADF2018.105\bin\intelmpi\bin;C:\ADF2018.105\bin\Putty;C:\ADF2018.105\msys\usr\bin;C:\ADF2018.105\bin\intelmpi\bin;C:\ADF2018.105\bin\Putty;C:\ADF2018.105\bin\TclTk\bin;C:\ADF2018.105\bin\openbabel;C:\ADF2018.105\bin;C:\windows\system32;C:\windows;C:\windows\System32\Wbem;C:\windows\System32\WindowsPowerShell\v1.0\;C:\windows\System32\OpenSSH\;C:\Program Files (x86)\Intel\Intel(R) Management Engine Components\DAL;C:\Program Files\Intel\Intel(R) Management Engine Components\DAL;C:\Program Files (x86)\Intel\Intel(R) Management Engine Components\IPT;C:\Program Files\Intel\Intel(R) Management Engine Components\IPT;C:\Program Files\Intel\WiFi\bin\;C:\Program Files\Common Files\Intel\WirelessCommon\;C:\Users\Fedor\AppData\Local\Microsoft\WindowsApps;
C:\ADF_DATA\CMA-ES-FIT\xyz>cmd
Microsoft Windows [Version 10.0.17134.345]
(c) 2018 Microsoft Corporation. Alle rechten voorbehouden.
C:\ADF_DATA\CMA-ES-FIT\xyz>sh
sh-4.3$
```

We now have a basic shell in which can do so some scripting

Functions we will use a lot: cat, ls, pwd, various commands inside \$ADFBIN

# Some scripting examples

<code>cat dog</code>	output contents of the file named dog to the screen
<code>cat file &gt; file2</code>	output contents of file to a new file, file2
<code>cat file2 &gt;&gt; file3</code>	output file2 and <b>append</b> to file3
<code>cat *.bgf &gt; geo</code>	output all files ending in .bgf to a new geo file
<code>cat geo &gt;&gt; ../geo</code>	output geo to the file geo in the directory below
<code>pwd</code>	show in which directory we are
<code>cd dog.results</code>	go one directory up to dog.results
<code>cd ..</code>	go one directory down
<code>cd -</code>	go to the directory you were in before
<code>ls</code>	show which files are in this directory
<code>ls -ltra</code>	show files in directory with more details, order to time



# Some other useful shell tips

arrow up / down    scroll through previous commands the directory below

for; do; done    Loop. Example:  
for i in 1 2 3; do cat \$i/geo >> geo; done  
(append 1/geo 2/geo and 3/geo to geo)

!?    reuse last argument. Example:  
ls geo  
cp !\$ geo.1 (== cp geo geo.1)

<TAB>    Autocomplete. Example: you want to copy trainset.in  
cp tr<TAB> will search for all files here starting with 'tr'  
if only 1: it completes to that, otherwise prints a list

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