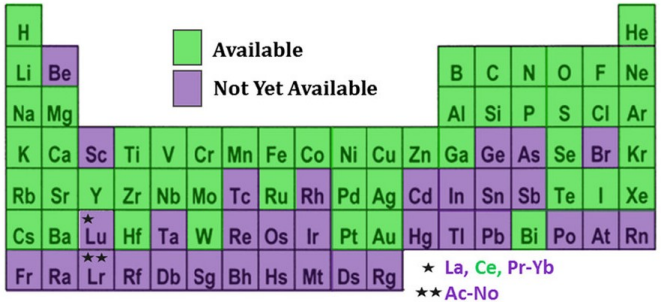
ReaxFF:
reactive molecular dynamics

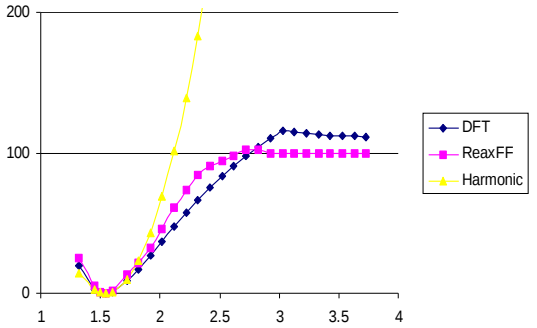
Ole Carstensen
carstensen@scm.com

DEFNET Workshop 3
March 23 | Gent

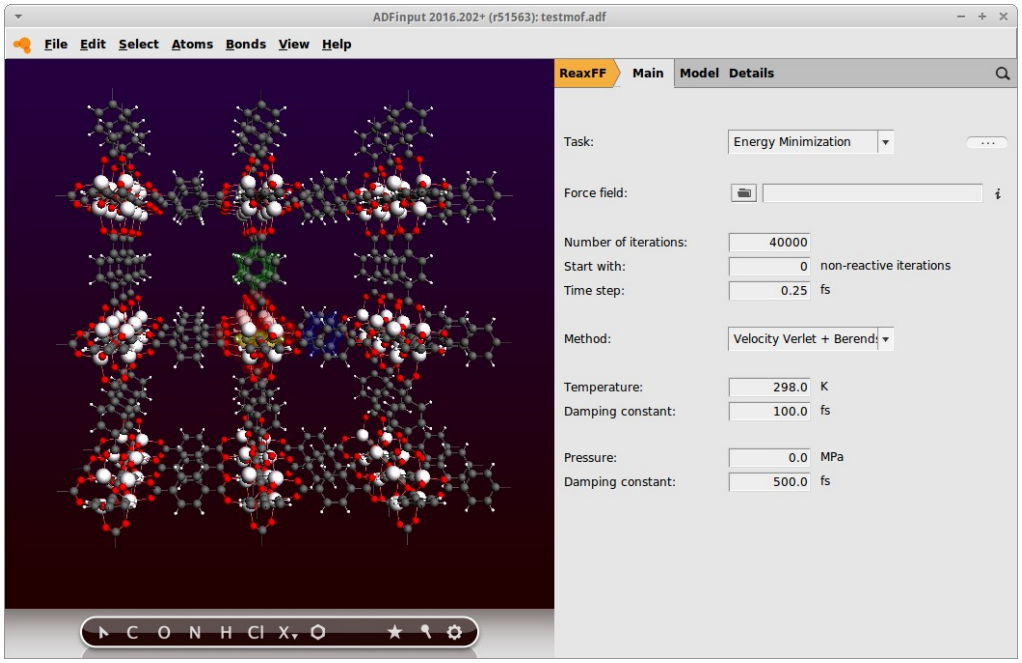
Outline

SCM
Software for Chemistry & Materials

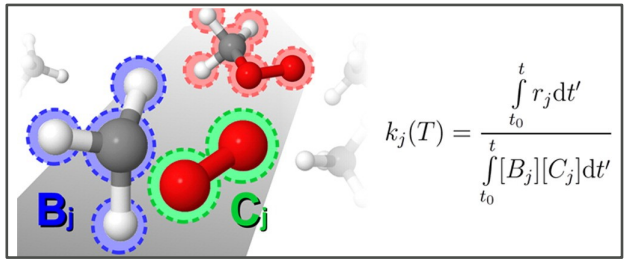


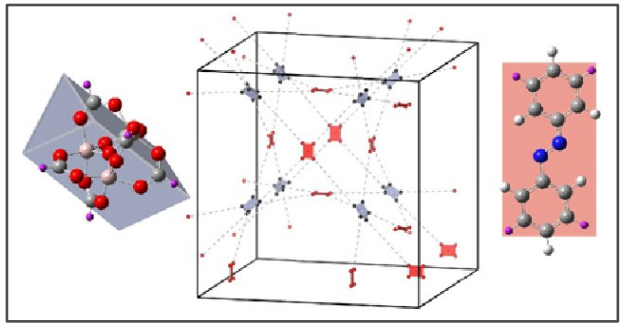


About SCM



General aspects



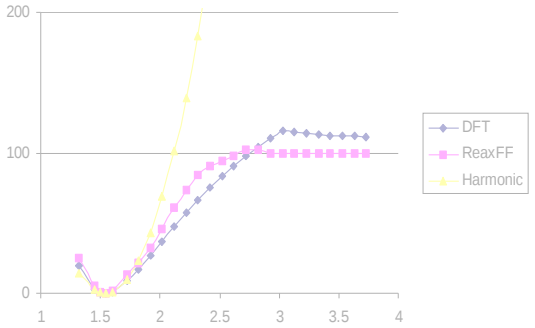


Selected features of SCM's ReaxFF

SCM

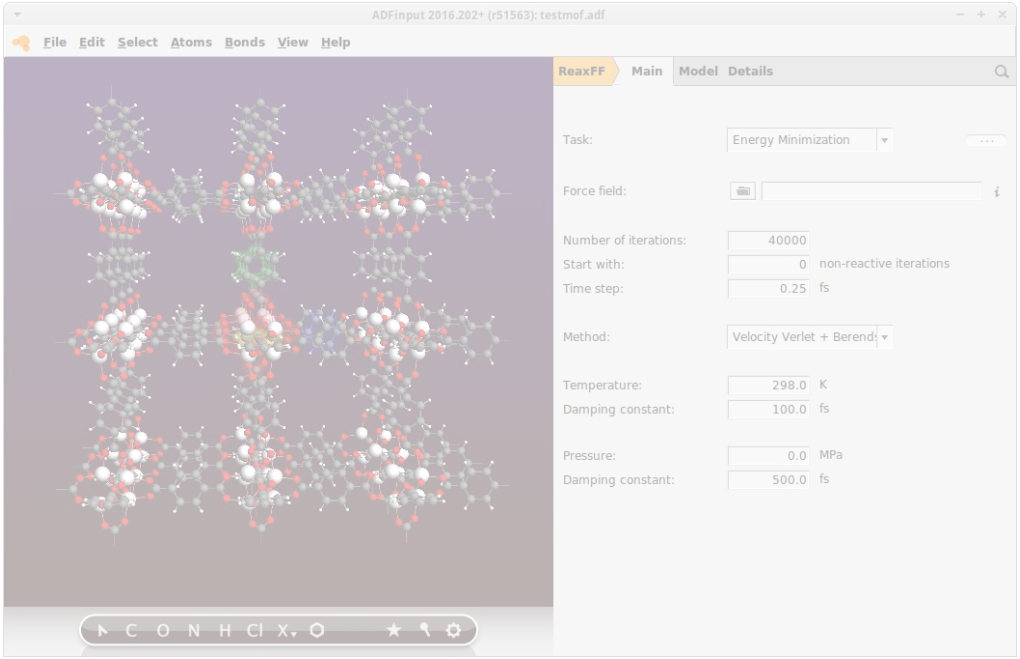
Outline

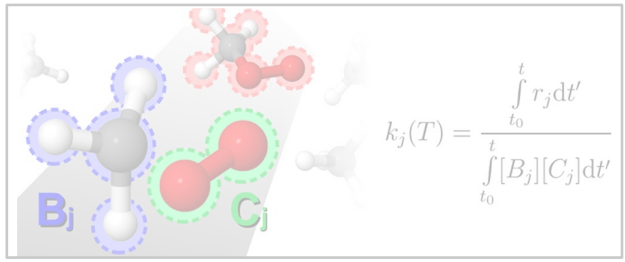
SCM
Software for Chemistry & Materials

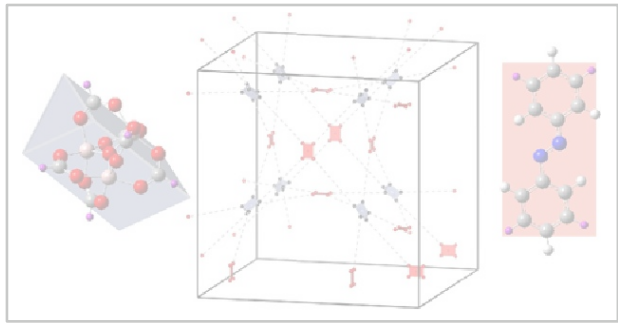


About SCM

General aspects







Selected features of SCM's ReaxFF

SCM

Background

Amsterdam Density Functional (ADF) Development

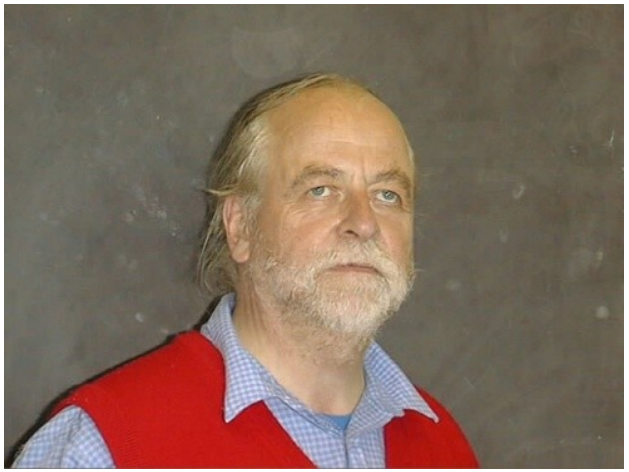
Baerends group VU, Amsterdam (>1973)
Ziegler group, Calgary (>1975)

SCM: Spin-off company (1995)

Development, testing, debugging, optimizing, porting, documentation, support, ..

Many academic collaborators / EU networks
(more than 90 authors)

Evert-Jan Baerends



Tom Ziegler
(1945-2015)

Overview: The ADF molecular modelling suite

ADF
powerful molecular DFT code
-Spectroscopy
- Heavy elements
- Analysis
- and more...

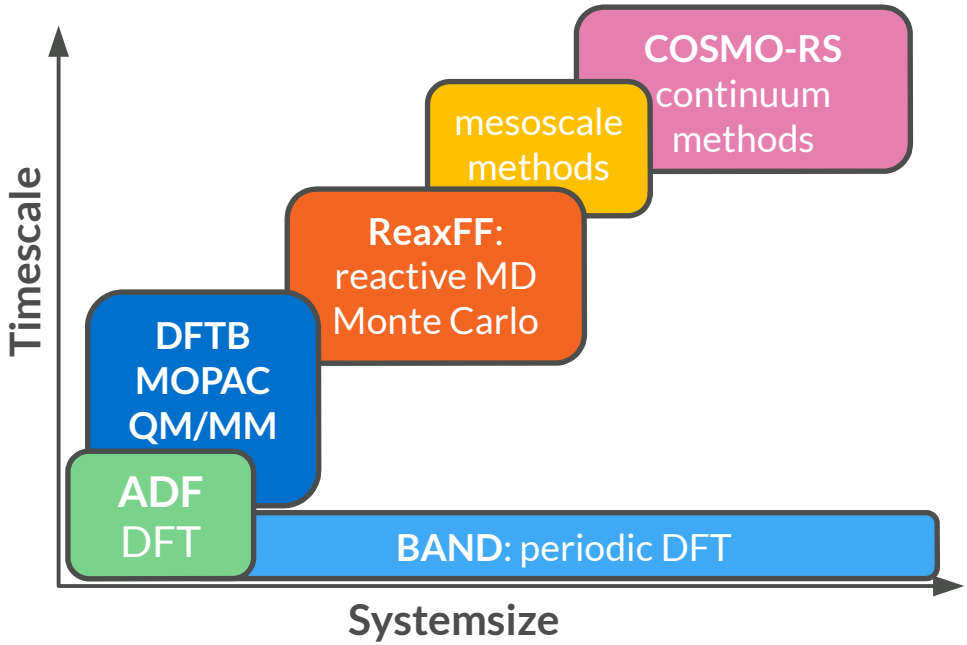
BAND
periodic DFT (1D,2D,3D)

DFTB
Fast approximate DFT

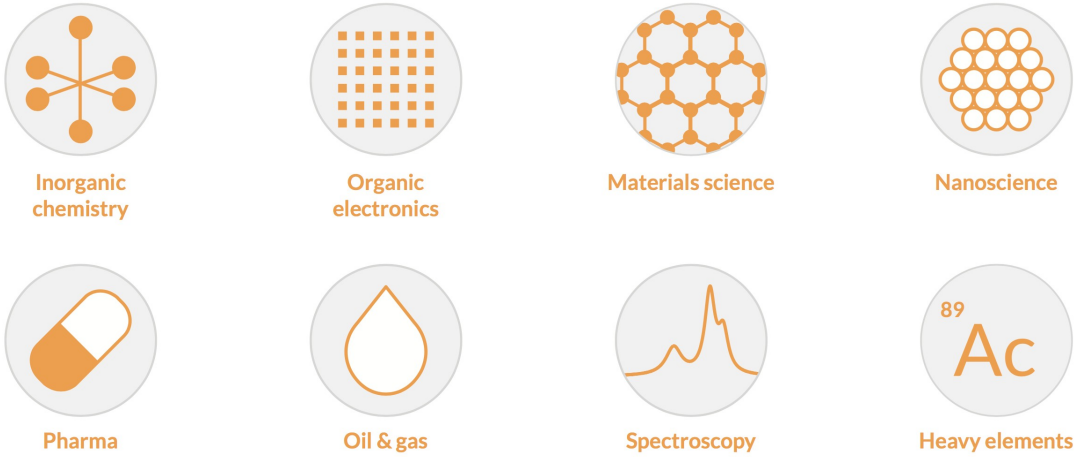
ReaxFF
Reactive Molecular Dynamics

COSMO-RS
Fluid thermodynamics

Scripting, Workflows



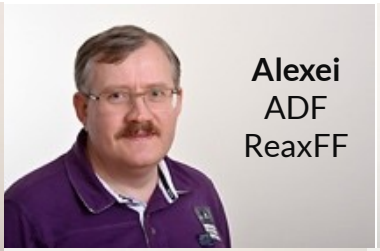
Key applications areas:



The SCM Team

Developers

Olivier
GUI



Alexei
ADF
ReaxFF

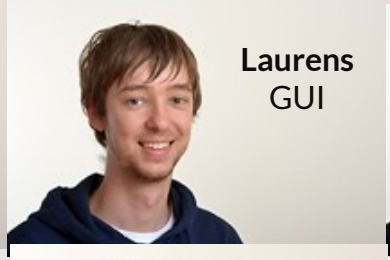
Erik
ADF
COSMO-RS

Pier
BAND

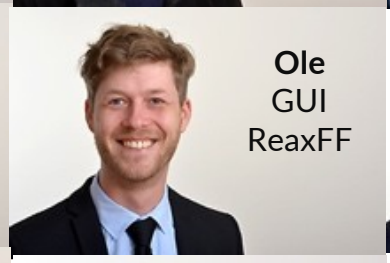
Mirko
ADF
BAND

Hans
Linux
GPU
Python

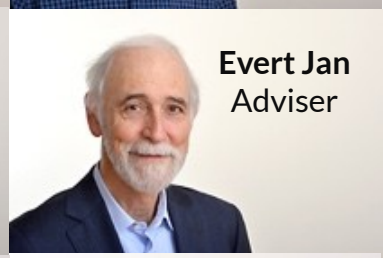
Thomas
DFTB
Scripting



Laurens
GUI



Ole
GUI
ReaxFF



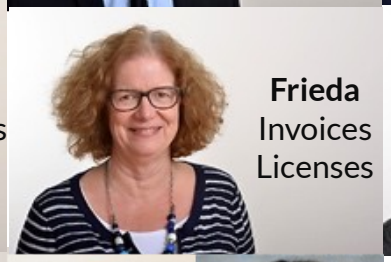
Evert Jan
Adviser

Business

Stan
CEO

Fedor
Marketing

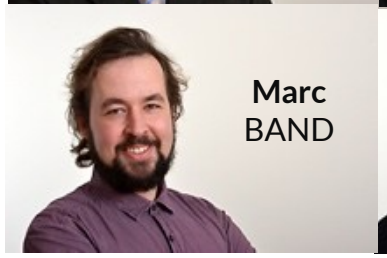
Sergio
Collaborations



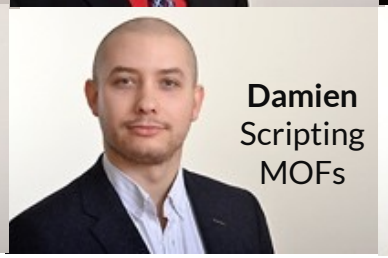
Frieda
Invoices
Licenses

Kitty
Finance

EU fellows



Marc
BAND



Damien
Scripting
MOFs

Anna
ReaxFF
MOFs

Michal &
Robert:
QM/MM &
excited
states MD

The SCM Team

Attending this workshop

ReaxFF Background

ReaxFF Development

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

Adri

Initial and ongoing development: Adri van Duin (Penn State University).

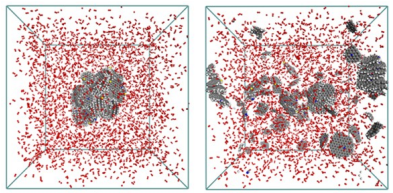
RxFF_CONSULTING

(ReaxFF-Parameters)

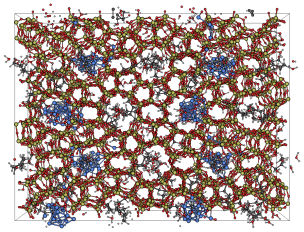
ReaxFF @ SCM

- *optimization & parallelization* of the original code.
- many parameters included (e.g. transition metals)
- GUI support
- Post-processing (reaction event detection)
- internal parameter optimization via Monte Carlo
- ...

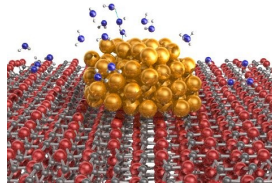
Selection of parallel SCM/ReaxFF studies:



Pyrolysis of an Illinois coal sample (Combustion & Flame 2012)



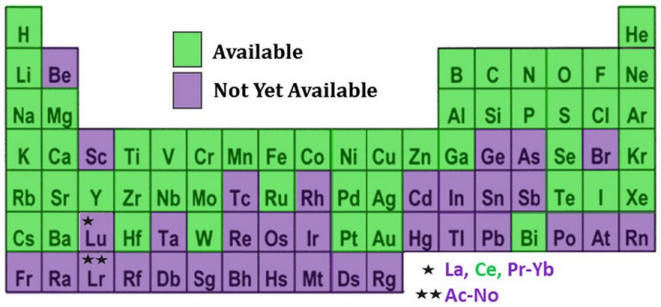
Hexane cracking on a Fe/H-ZSM5 catalyst (Fe/O: Aryanpour et al., JPC-A 2010)

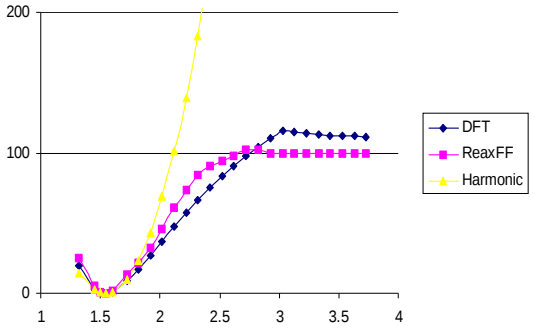


Cu-metal particle on a ZnO-support with water vapor (Zn/O: Raymand et al., Surf. Sci. 2010)

Outline

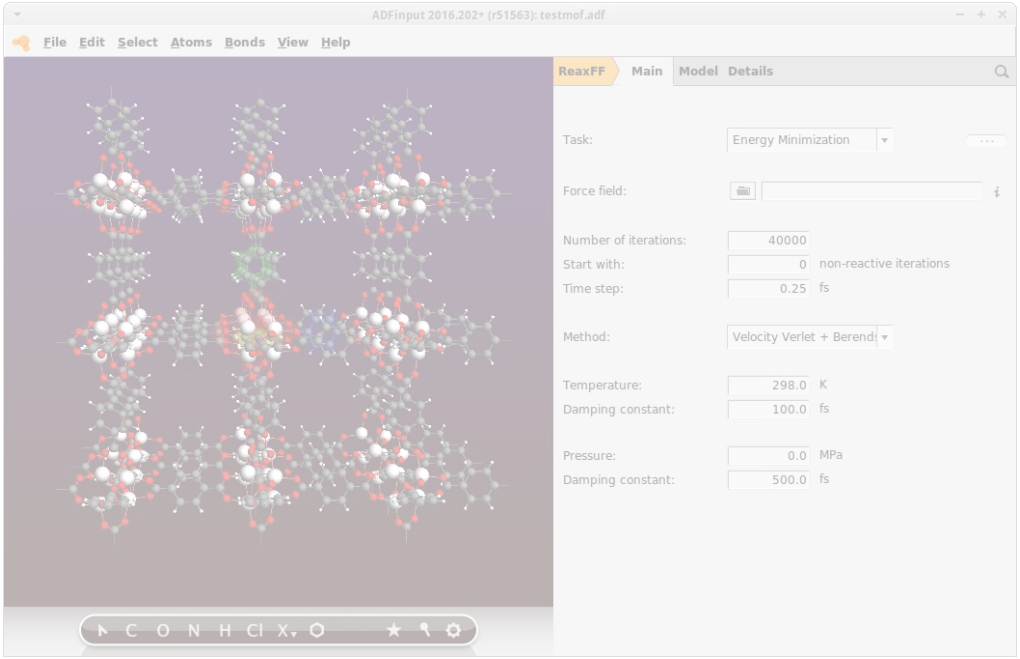
SCM
Software for Chemistry & Materials

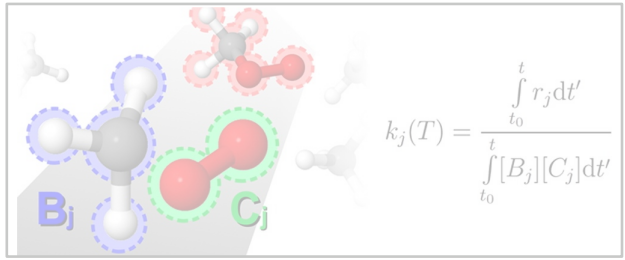


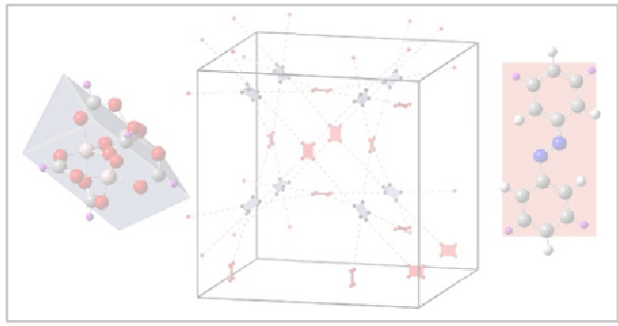


About SCM

General aspects







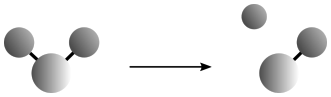
Selected features of SCM's ReaxFF

SCM

Why reactive molecular dynamics?

"The study of change of matter (chemical reactions) and synthesis lies at the heart of chemistry [...]"

Wikipedia contributors, "Comparison of chemistry and physics," Wikipedia, The Free Encyclopedia (accessed March 16, 2016).

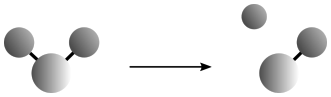


Simulating chemistry: Forming and breaking of bonds is rather essential...

Why reactive molecular dynamics?

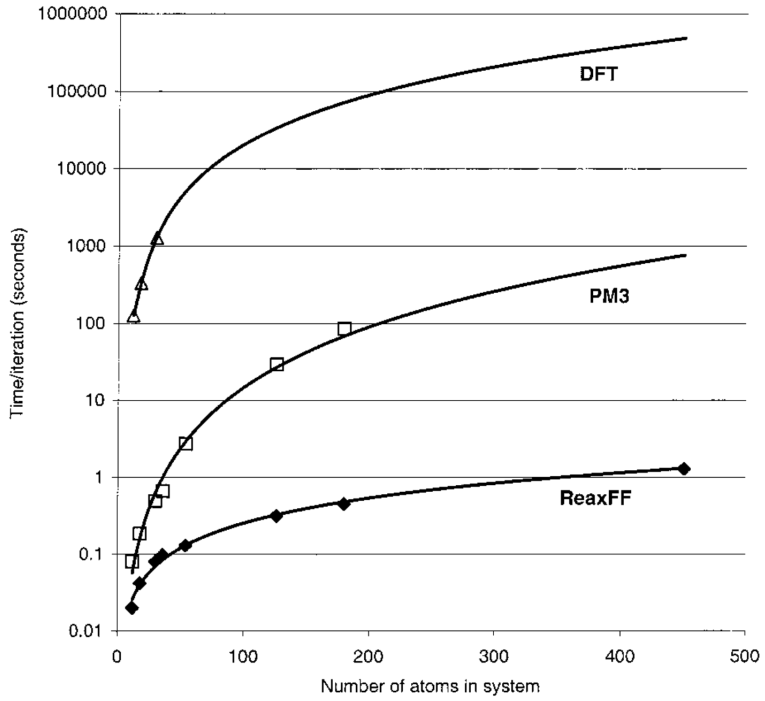
"The study of change of matter (chemical reactions) and synthesis lies at the heart of chemistry [...]"

Wikipedia contributors, "Comparison of chemistry and physics," Wikipedia, The Free Encyclopedia (accessed March 16, 2016).



Simulating chemistry: Forming and breaking of bonds is rather essential...

Speed: (scaling) non-reactive MD —(~10-50 times faster)→ **ReaxFF** (NlogN) —(~1 000 000 times faster)→ QM (conventional DFT) (N^3 or worse)

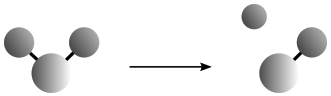


A. C. T. van Duin *et al. J.Phys. Chem. A* **2001**, 105, 9396-9409.

Why reactive molecular dynamics?

"The study of change of matter (chemical reactions) and synthesis lies at the heart of chemistry [...]"

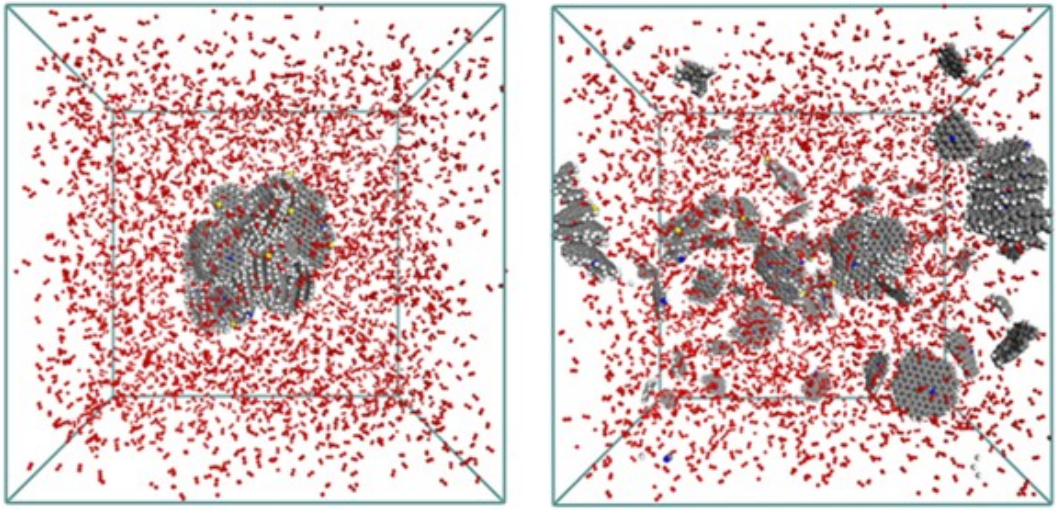
Wikipedia contributors, "Comparison of chemistry and physics," Wikipedia, The Free Encyclopedia (accessed March 16, 2016).



Simulating chemistry: Forming and breaking of bonds is rather essential...

Speed: (scaling) non-reactive MD —(~10-50 times faster)→ **ReaxFF** (NlogN) —(~1 000 000 times faster)→ QM (conventional DFT) (N^3 or worse)

Char combustion with ReaxFF: 250 ps, **>35 000 Atoms**

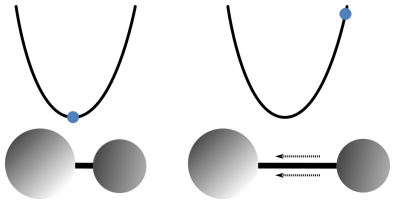


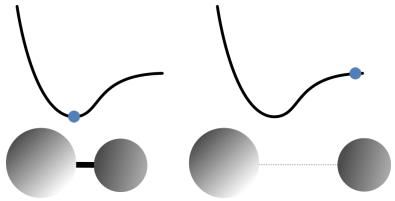
F. Castro-Marcano *et al*, *Combustion and Flame* **2012**, 159(3), 1272-1285.

Because: The simulation of complex and huge - really huge - systems becomes possible.

ReaxFF – The concept...

Standard forcefields **vs** *ReaxFF*



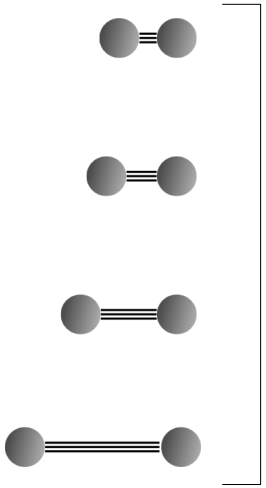


Harmonic potentials based on atom distance, bond breaking impossible, e.g.

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

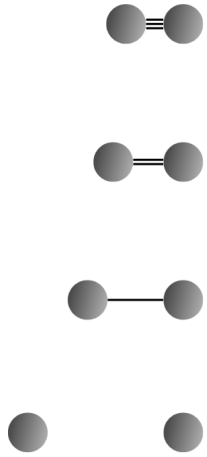
Non-harmonic potentials based on bond orders, bond breaking/forming possible, e.g.

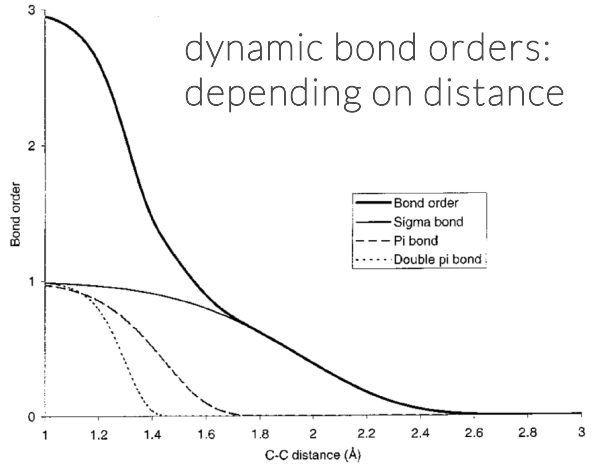
$E_{bond} \propto -(bond\ order) \times \exp[\ (1 - bond\ order)\ ]$



($E_{bond} \rightarrow \infty$)

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





dynamic bond orders: depending on distance

($E_{bond} \rightarrow 0$)

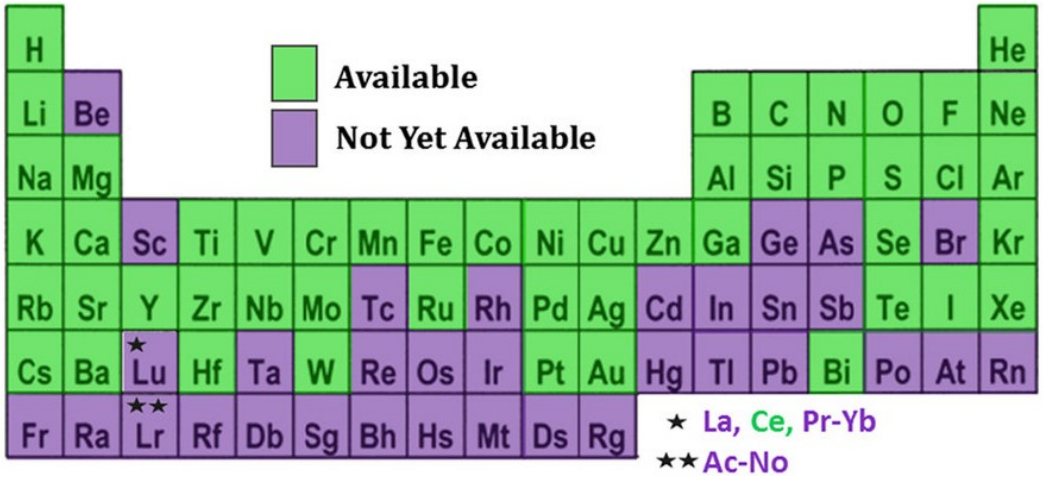
A.C.T. van Duin *et al*,*J. Phys. Chem. A* **2001**, 105, 9396-9409.

ReaxFF – Applicability

Q: Can I use ReaxFF for my system?
A: Yes, but you will need a *set of suitable parameters*.

Parametersets included in ADF:

ADF 2013: 17 sets, 19 elements
ADF 2014: 38 sets, 29 elements
ADF 2016: 58 sets, 39 elements

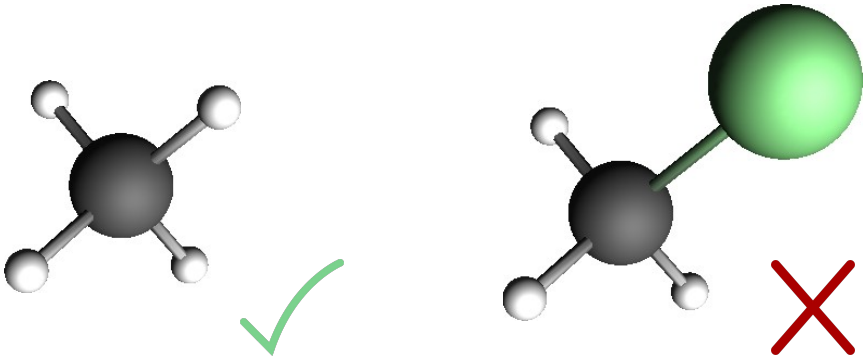


A.C.T. van Duin *et al npj Computational Materials* **2016**, 15011.

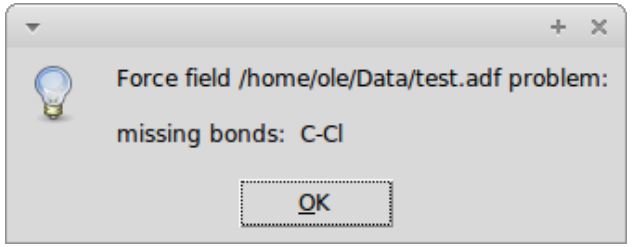
But:

Bonded terms for each pair are needed.

e.g. `FeOCHCl.ff`



Automatic checks



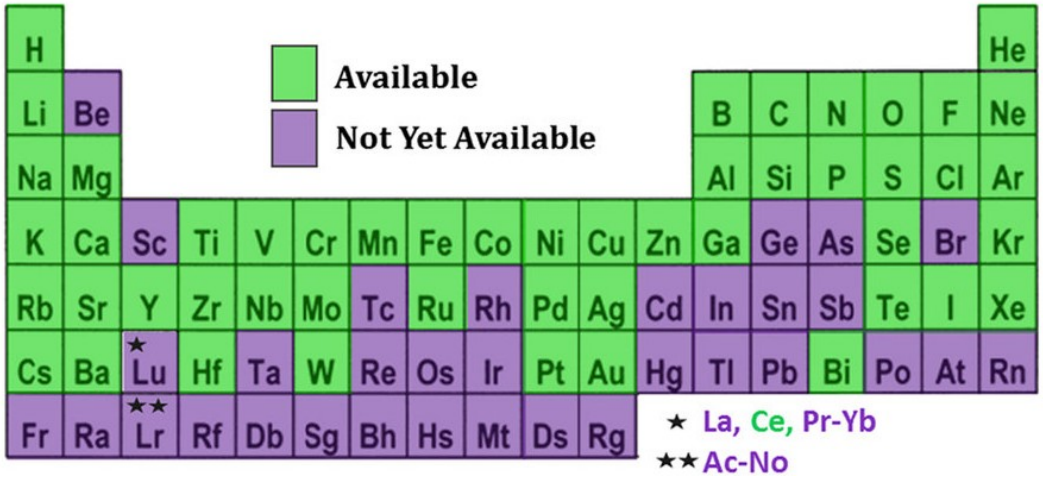
https://www.scm.com/documentation/ReaxFF/Included_Forcefields/

ReaxFF – Applicability

Q: Can I use ReaxFF for my system?
A: Yes, but you will need a *set of suitable parameters*.

Parametersets included in ADF:

ADF 2013: 17 sets, 19 elements
ADF 2014: 38 sets, 29 elements
ADF 2016: 58 sets, 39 elements

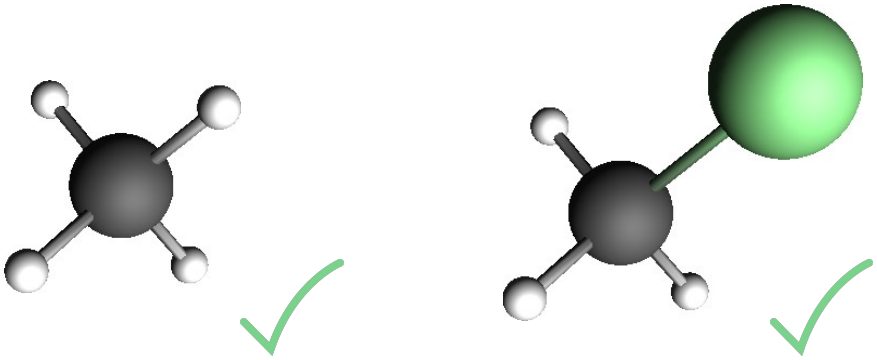


A.C.T. van Duin *et al npj Computational Materials* **2016**, 15011.

But:

Bonded terms for each pair are needed.

e. g. ~~`FeOCHCl.ff`~~ `CHONSMgPNaCuCl.ff`



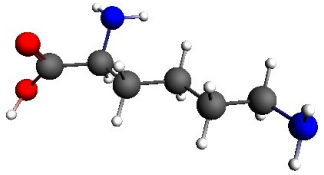
Somtimes using a different parameterset does the trick...

https://www.scm.com/documentation/ReaxFF/Included_Forcefields/

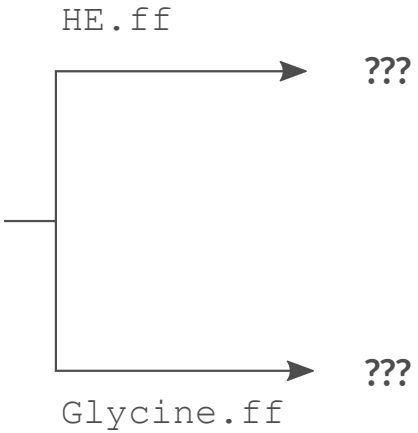
ReaxFF – Applicability

Q: What about the quality and transferability of parameters?
A: Well, that depends on several aspects...

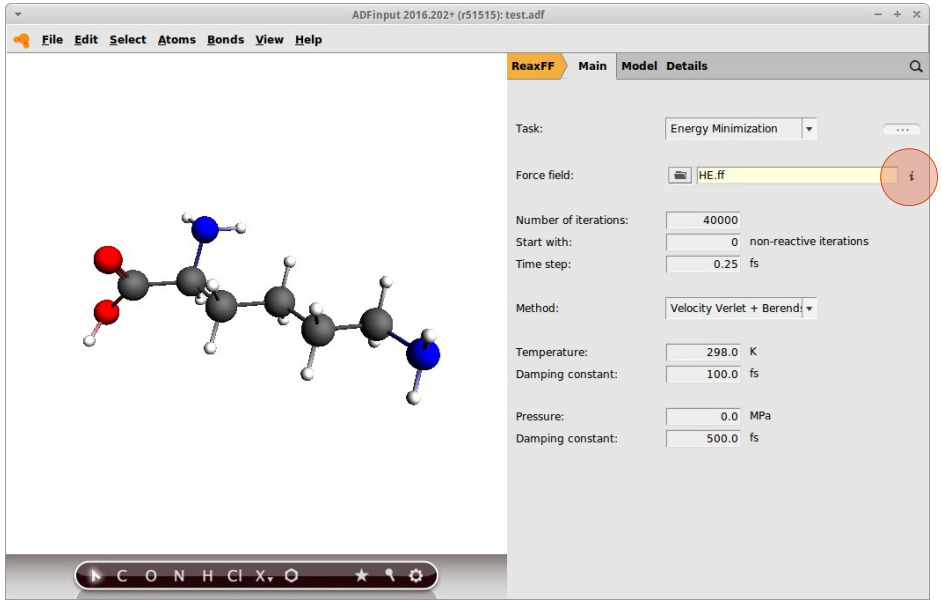
- their initial purpose



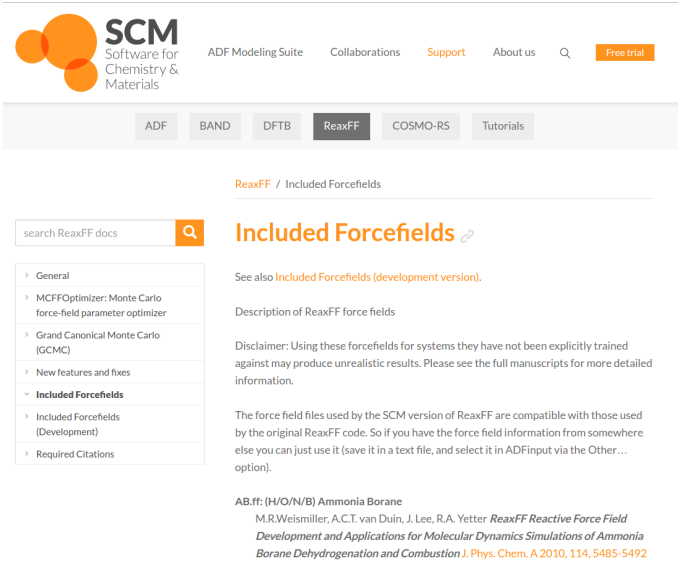
System:
Lysine, ambient conditions...



Check the references via GUI or online...



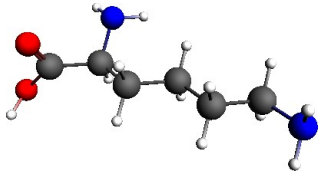
https://www.scm.com/documentation/ReaxFF/Included_Forcefields/



ReaxFF – Applicability

Q: What about the quality and transferability of parameters?
A: Well, that depends on several aspects...

- their initial purpose



System:
Lysine, ambient conditions...

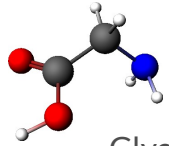
HE.ff

Purpose:
Hydrazine combustion at high T
...- awesome rocket science,
but in this case a bad choice.

source:
http://mediaarchive.ksc.nasa.gov/detail.cfm?mediaid=41220

Glycine.ff

Purpose:
Glycine, solvent effects and tautomerization
...- a reasonable choice

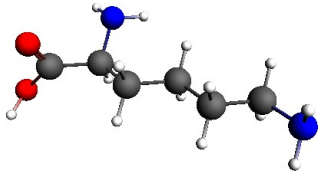


Glycine

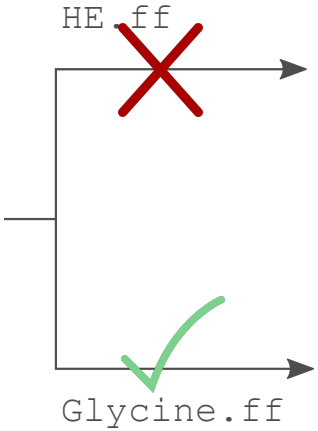
ReaxFF – Applicability

Q: What about the quality and transferability of parameters?
A: Well, that depends on several aspects...

- their initial purpose



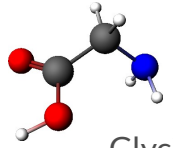
System:
Lysine, ambient conditions...



Purpose:
Hydrazine combustion at high T
...- awesome rocket science,
but in this case a bad choice.

source:
http://mediaarchive.ksc.nasa.gov/detail.cfm?mediaid=41220

Purpose:
Glycine, solvent effects and tautomerization
...- a reasonable choice



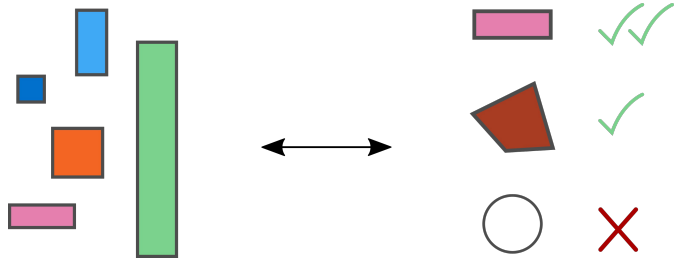
Glycine

- their (QM) training data

Your molecule is included in the training data. ✓✓

Your molecule is similar to those in the training data. ✓

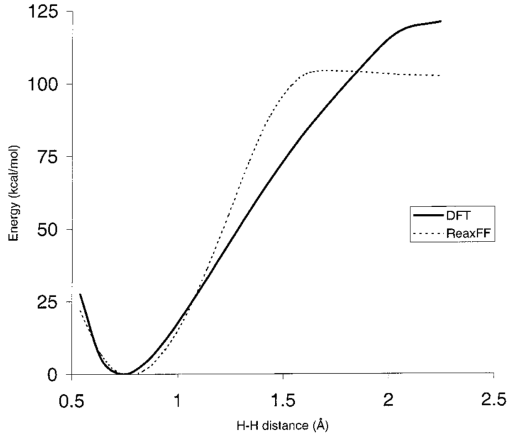
Your molecule is completely different from those in the training data. ✗



Training data Your system

Typical quality (best case)

"Qualitatively correct. Slightly better than semiempirics but not as good as DFT"
- Ole's rule of thumb



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

ReaxFF – Applicability

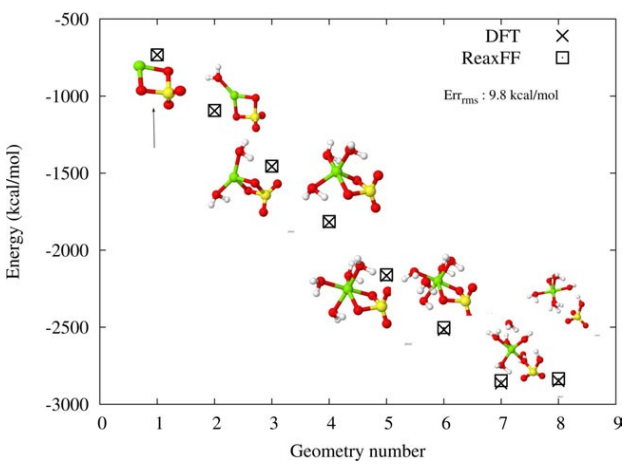
Q: Where can I get new ReaxFF Parameters for my system?
A: Sources of ReaxFF Parameters are...

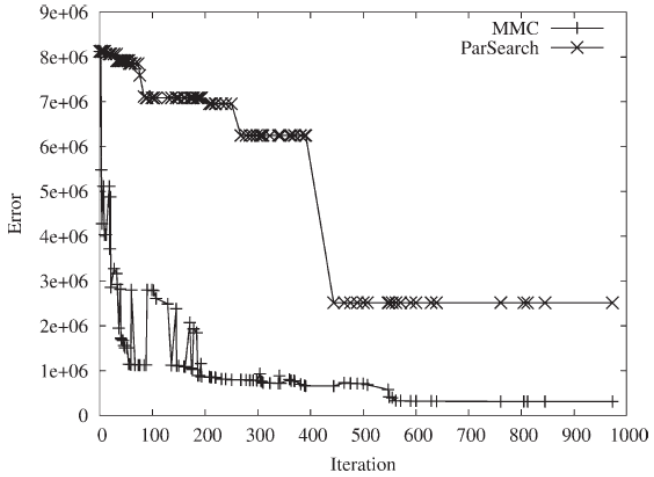
Academic research groups:
van Duin, Goddard, Hartke and others

Commercial Force Field-development:

RxFF_CONSULTING

MCFFOptimizer: Monte Carlo force-field parameter optimizer
(included in the ADF-molecular modelling suite)





Global Optimization Problem

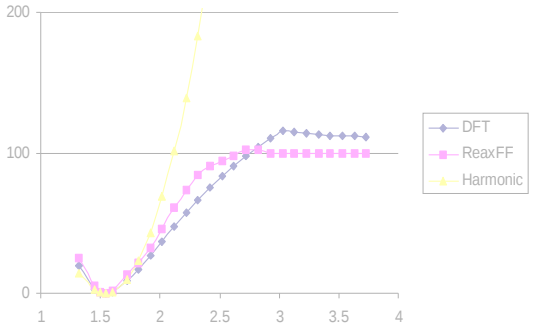
- Monte Carlo Walk in (huge) parameter space
- parameters are non-intuitive
- choosing your training data is crucial
- still an expert option

E. Iype *et al*, J. Comp. Chem. **34**, 1143-1154 (2013)

SCM

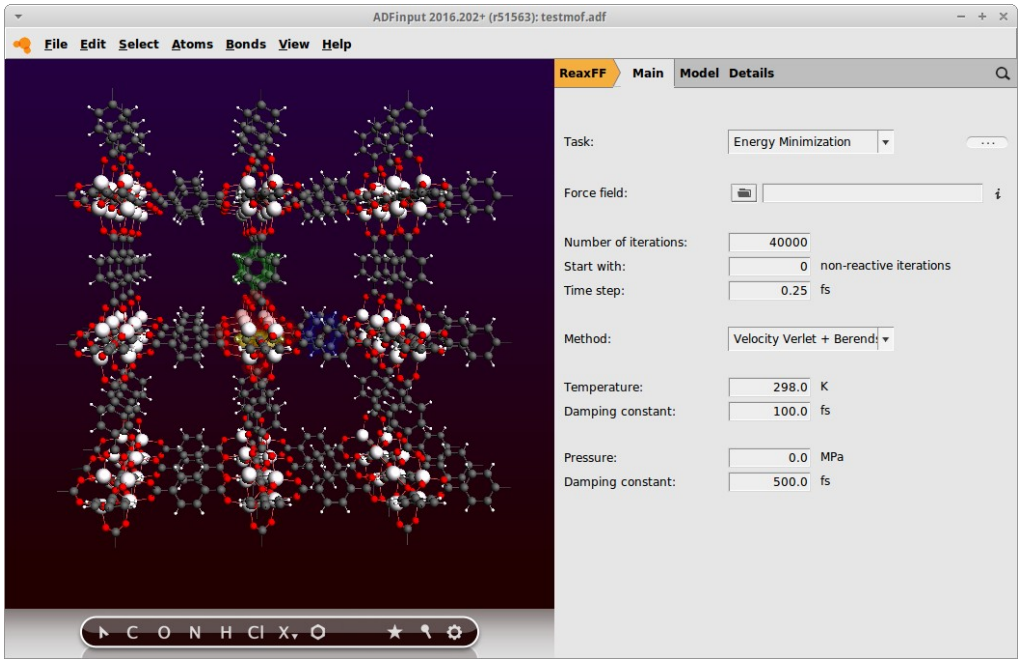
Outline

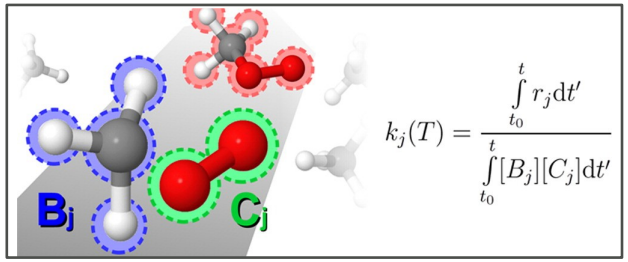
SCM
Software for Chemistry & Materials

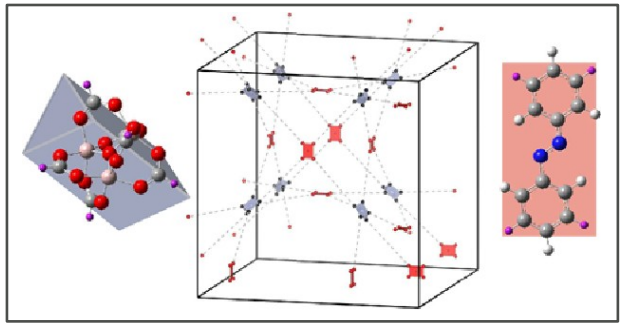


About SCM

General aspects



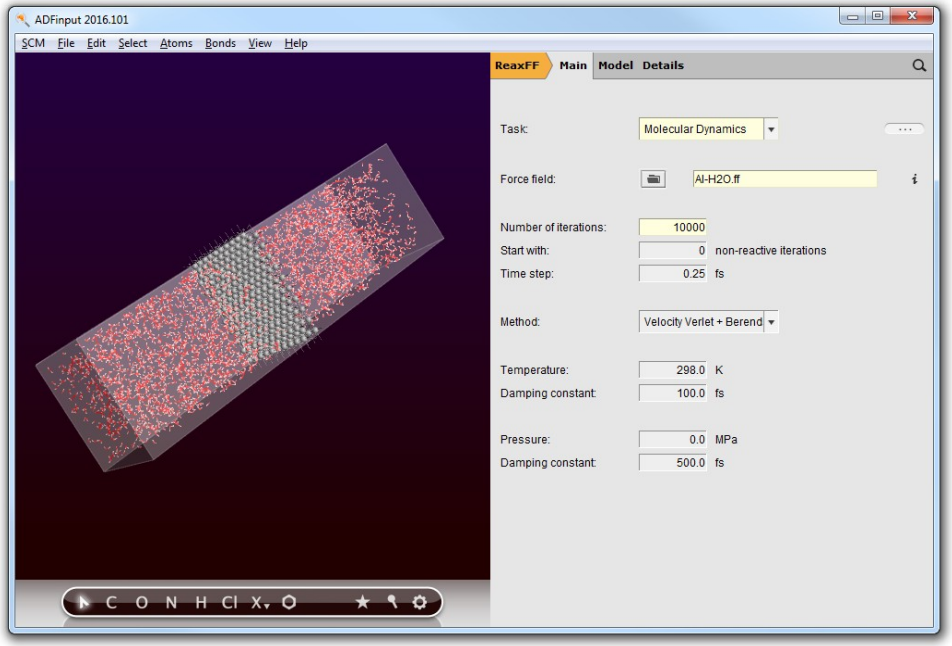


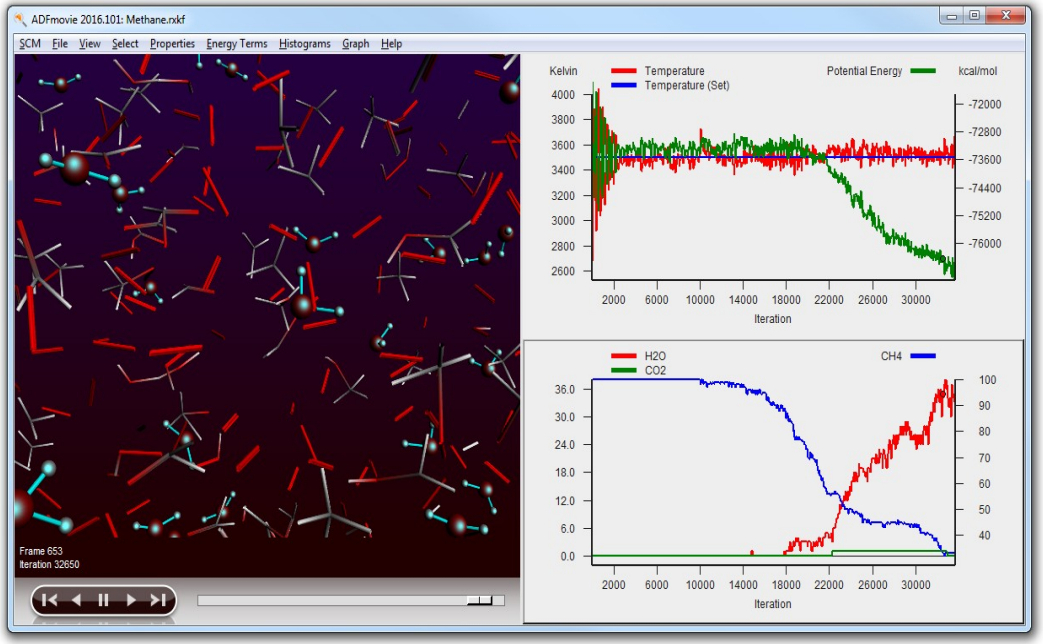


Selected features of SCM's ReaxFF

SCM

ReaxFF - GUI support





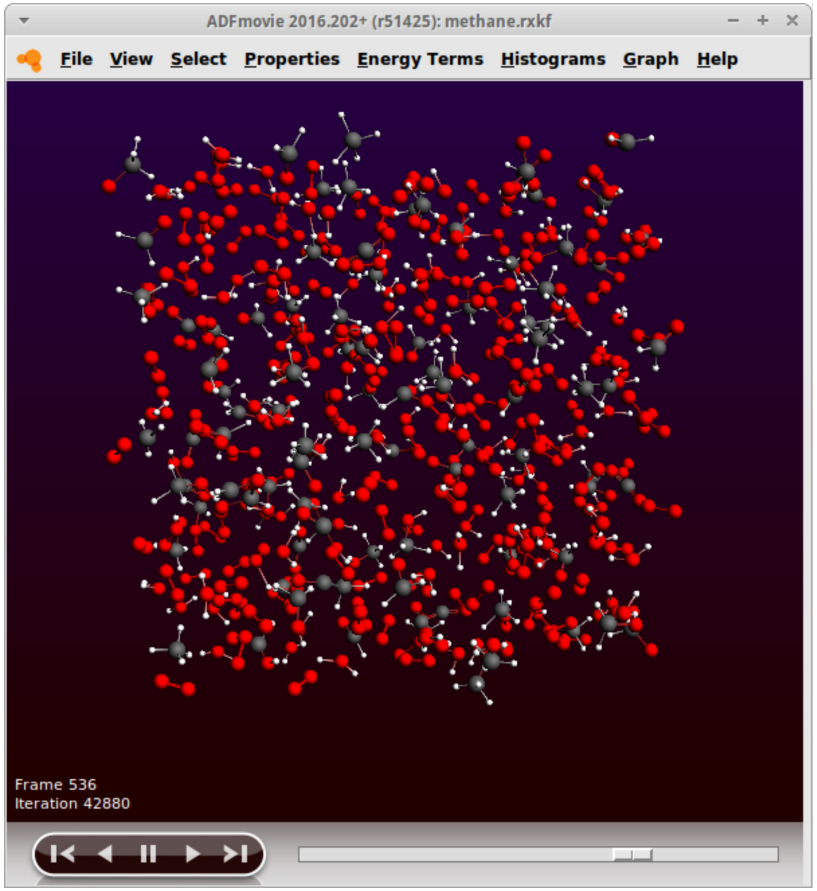
- ☑ Mac, Linux, Windows
- ☑ Easy setup
- ☑ Job management (local and remote)
- ☑ Visualization
- ☑ Analysis

Try it yourself in todays hands-on session!

SCM

ReaxFF – Reaction Event Detection

Chemical Trajectory Analyzer - ChemTraYzer



Methane combustion:
A simple reaction?

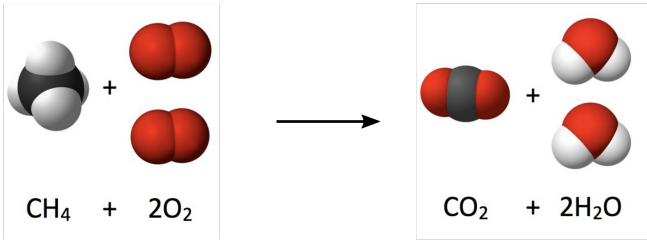
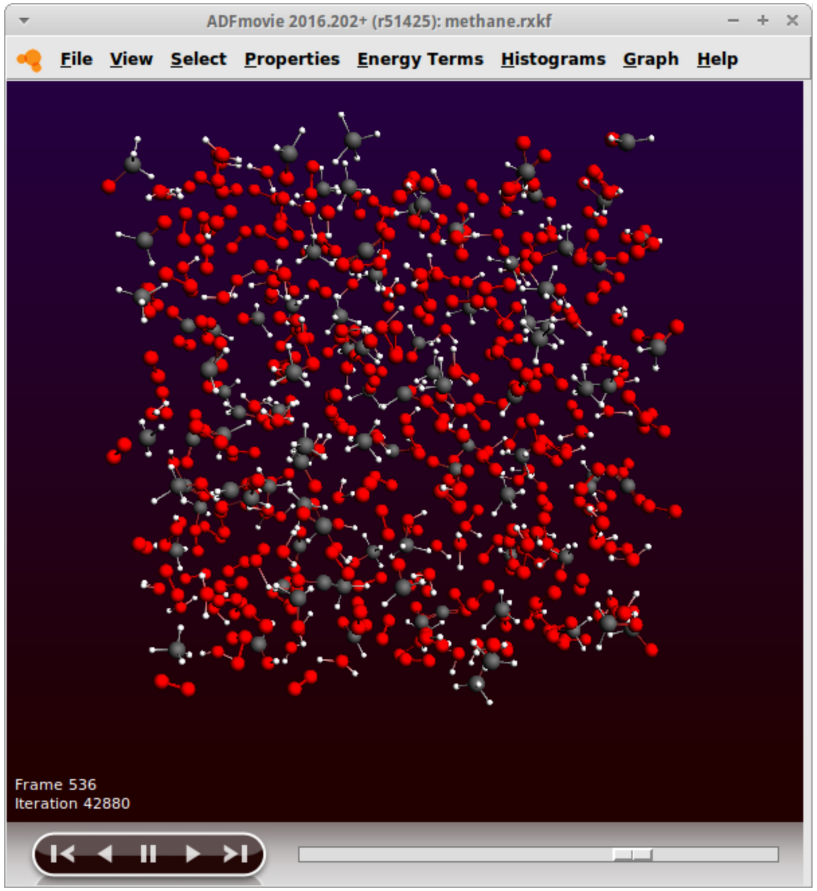


Image by Jynto Robert A. Rohde Jacek FHJynto
https://commons.wikimedia.org/w/index.php?curid=24953730

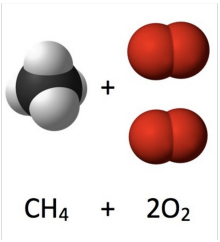
M. Döntgen et al., J. Chem. Theory Comp. **11**, 2517–2514 (2015)

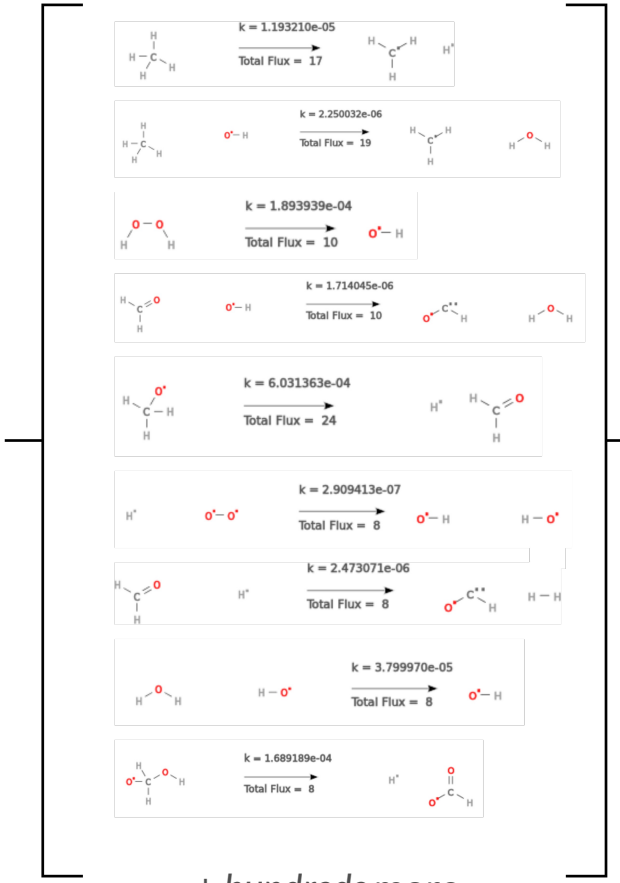
ReaxFF – Reaction Event Detection

Chemical Trajectory Analyzer - ChemTraYzer

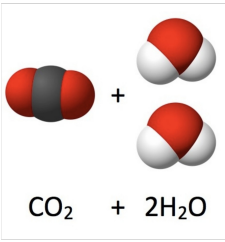


Complex reaction network





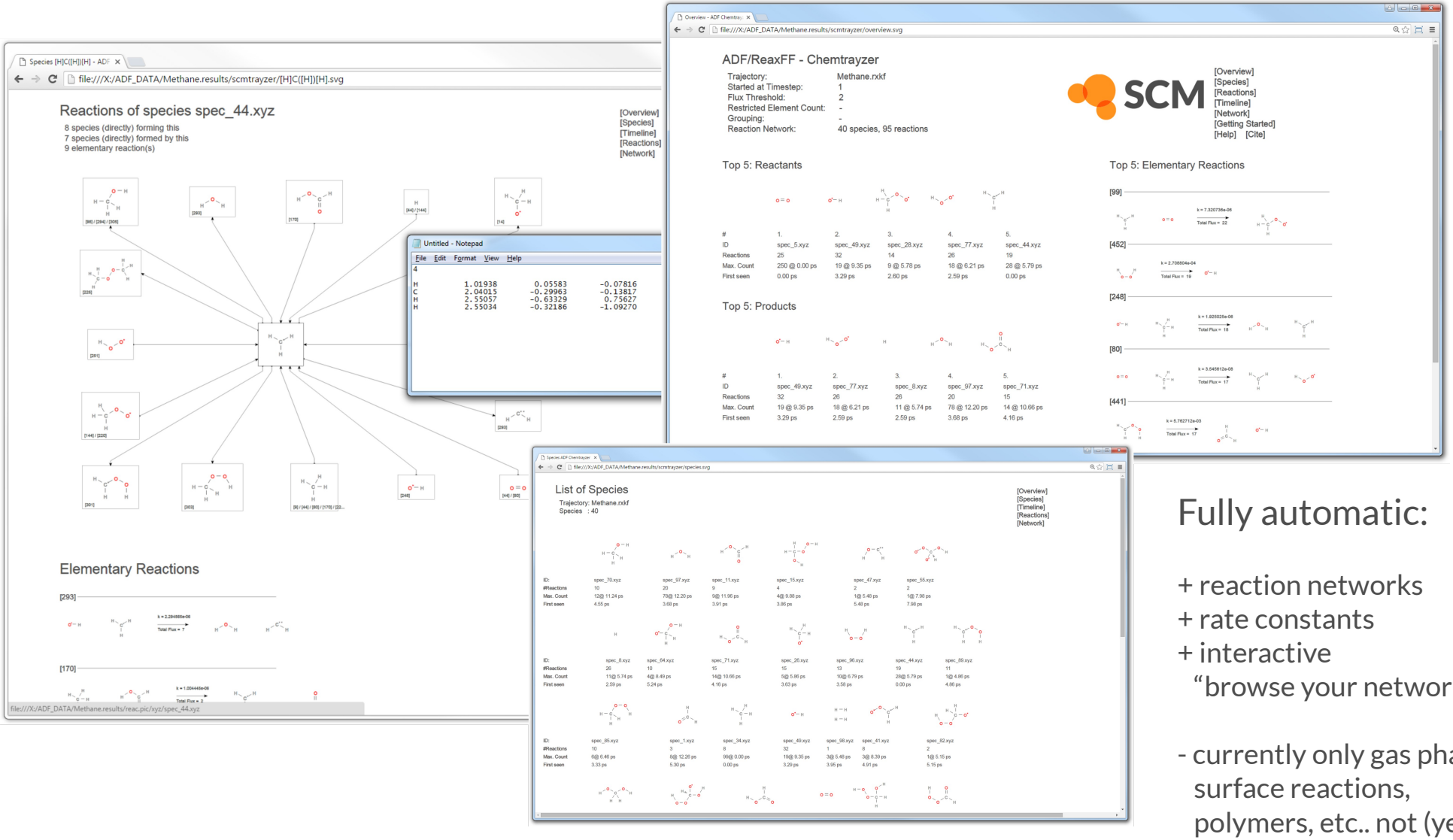
+ hundreds more...



M. Döntgen et al., J. Chem. Theory Comp. **11**, 2517–2514 (2015)

ReaxFF – Reaction Event Detection

Chemical Trajectory Analyzer - ChemTraYzer



Fully automatic:

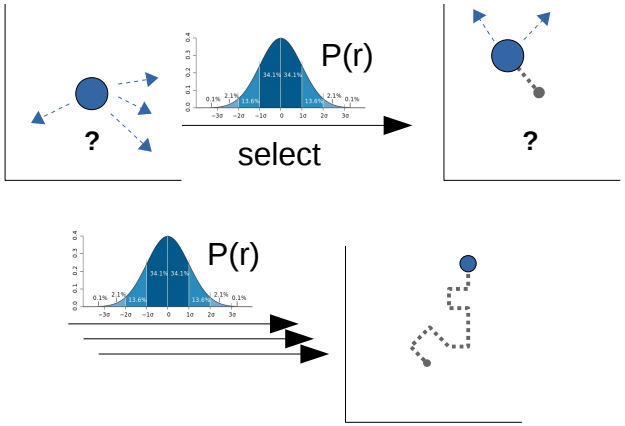
+ reaction networks
+ rate constants
+ interactive
  "browse your network"

- currently only gas phase surface reactions, polymers, etc.. not (yet!) supported

M. Döntgen et al., J. Chem. Theory Comp. **11**, 2517–2514 (2015)

New Acceleration Technique:
force-bias Monte Carlo (fbMC)

Metropolis Monte Carlo

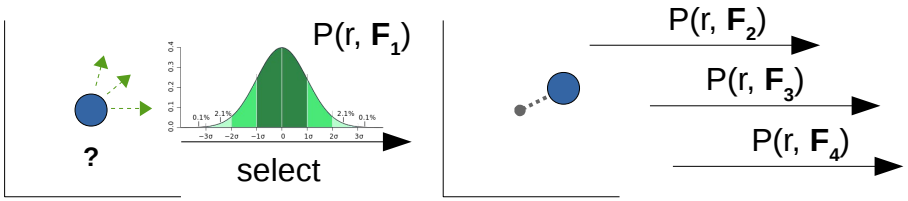


Sampling structural *Phase Space*

according to *one* well known
ensemble distribution function (e.g. NVT)

vs.

force-bias Monte Carlo



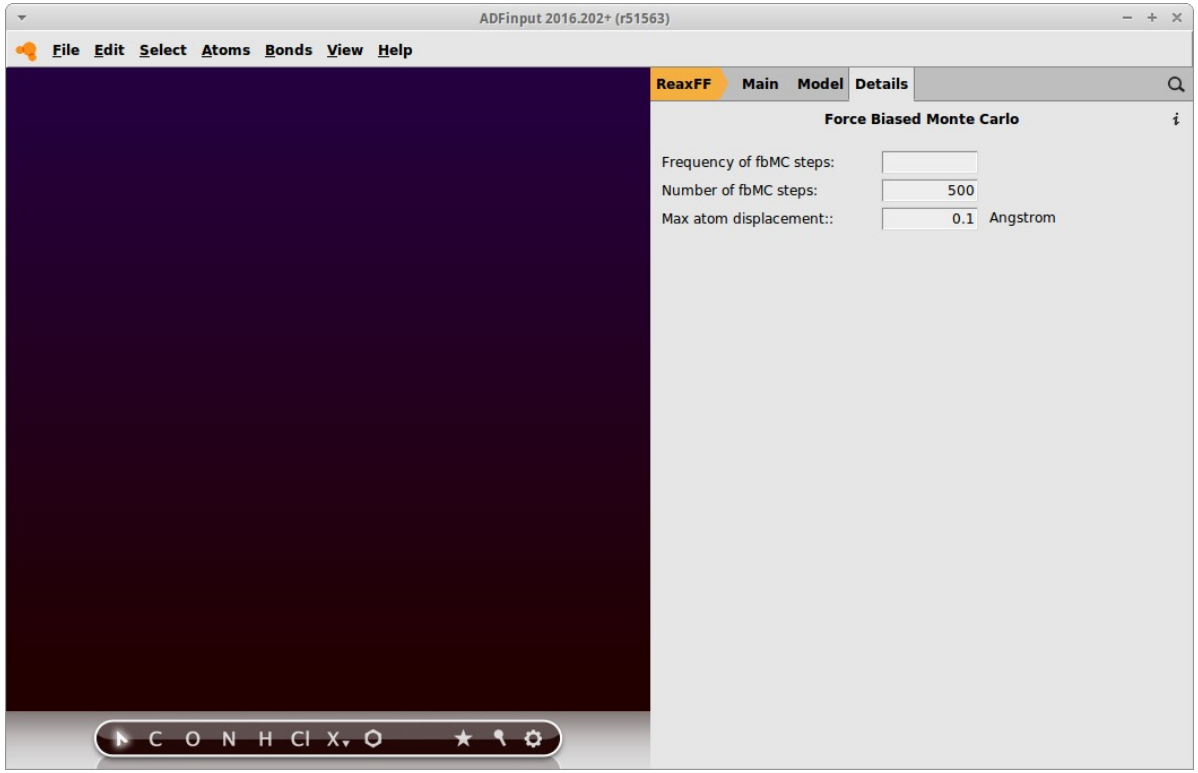
Sampling the *Dynamics*

- each change driven by "instantaneous" and "local" Boltzmann Distributions
- irrespective from distance to equilibrium
- Limits of P(r,F)
  T >> F → completely random movement
  T << F → Particle moves exactly in direction of force

Timonova *et al. Phys. Rev. B* **81**, 144107.
Mees *et al. Phys. Rev. B* **85**, 134301.

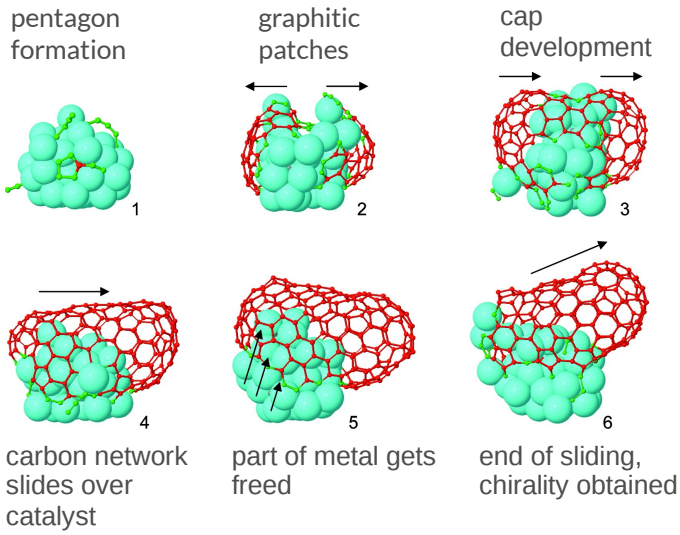
New Acceleration Technique:
force-bias Monte Carlo (fbMC)

GUI support

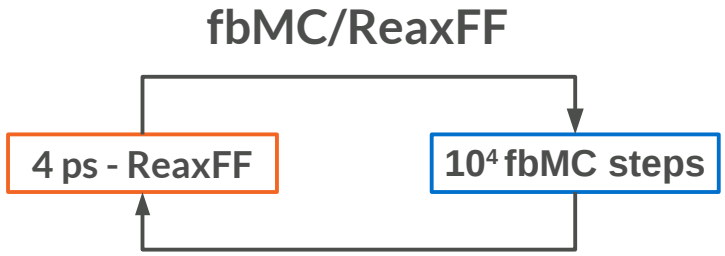


(surprisingly simple to use)

Successfully used in study of carbon nanotube growth



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



fbMC + ADF/ReaxFF dynamics:

Model the dynamics of processes that occur on loooong timescales by *MC sampling of the dynamics*

AuToGraFS

Automatic Topological Generator for Framework Structures

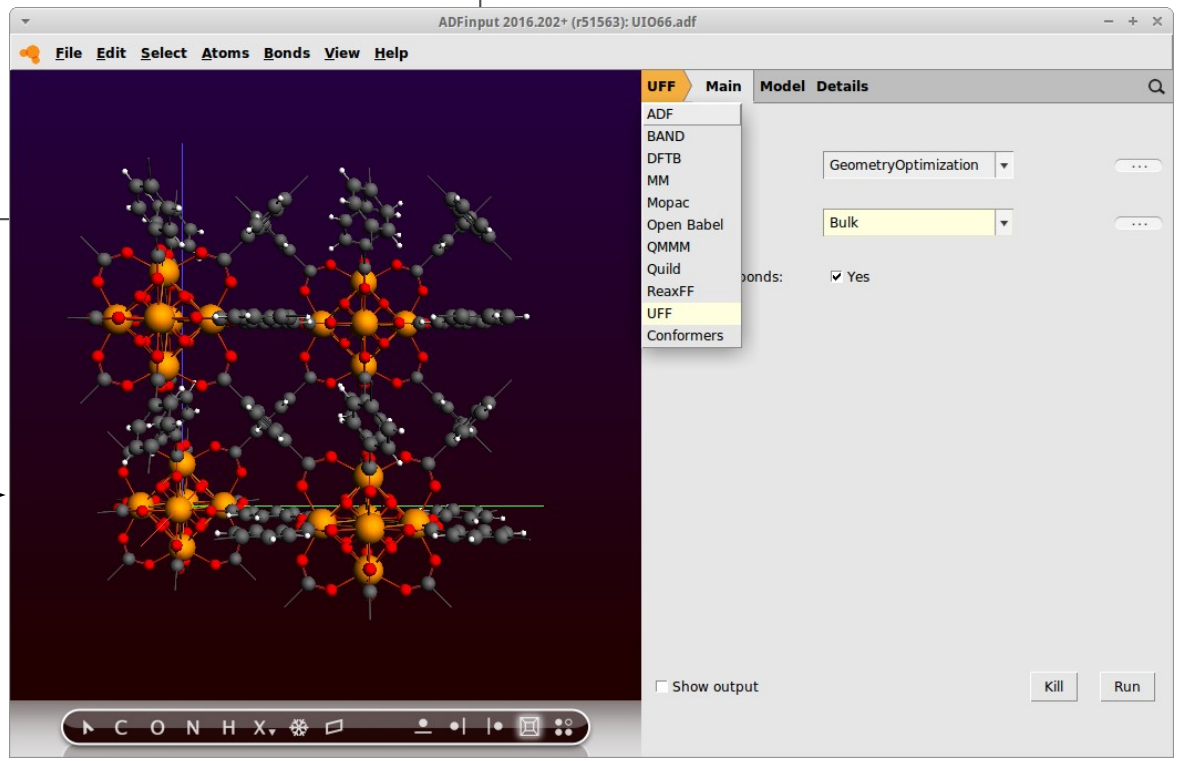
Example input: generate “UiO 66”

```
1. Topology: sqc19
   (center: icosahedral, linker: linear)

2. Center: Zr6-CO2_12

3. Linker:Benzene
```

AuToGraFS
(Blackbox)



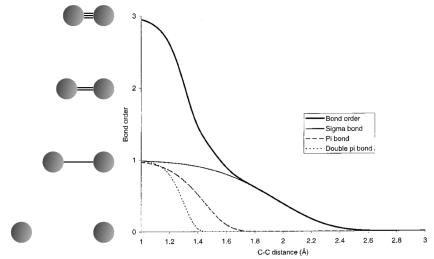
Included in ADF2016 as commandline tool. GUI support now under way...

M.A. Addicoat, D. Coupry, T. Heine *J. Phys. Chem. A* **2014**, 118, 9607−9614.

Summary

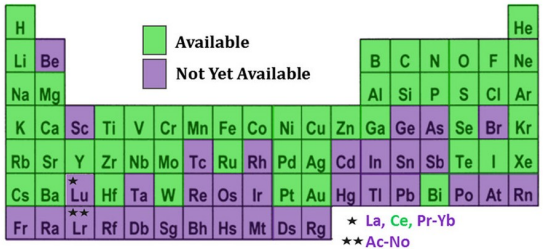
General aspects

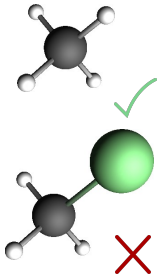
Key concept: Bond orders



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

Choosing parameters: sometimes tricky

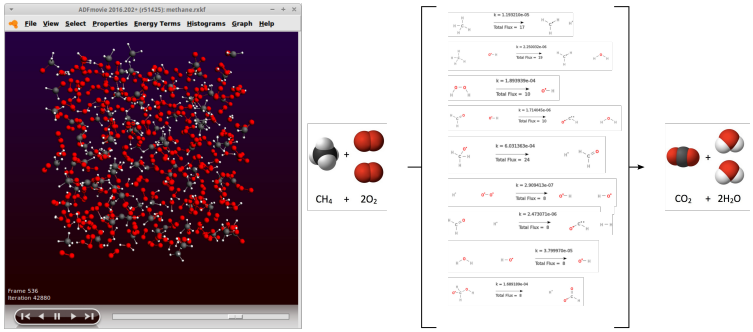




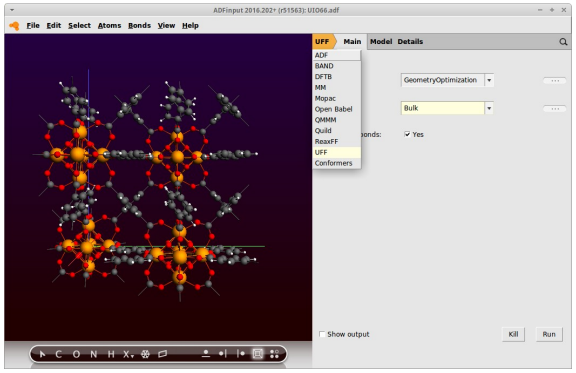
http://mediaarchive.ksc.nasa.gov/detail.cfm?mediaid=41220

(Creating new parameters: always tricky.)

Selected features



Automatic Reaction Detection



AuToGraFS

force-biasMC/ReaxFF

Acceleration Technique

SCM

contact us:

Licenses	**license@scm.com**
General information	**info@scm.com**
User support	**support@scm.com**