Introduction to ReaxFF:
Reactive Molecular Dynamics

Ole Carstensen
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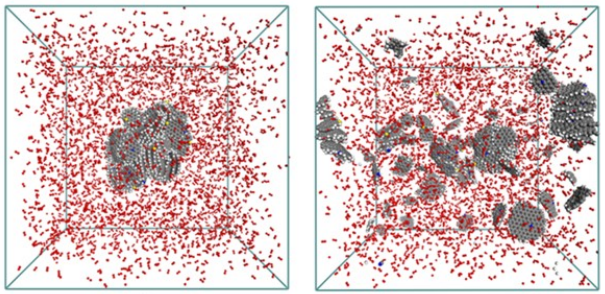
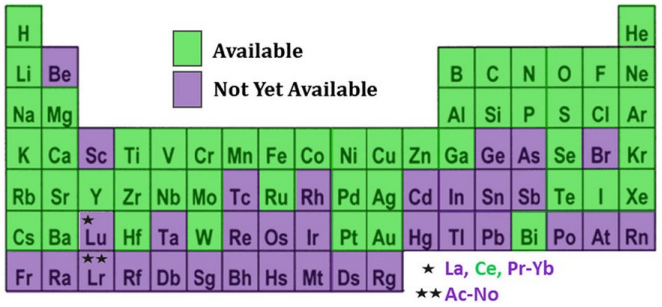
TCCM ADF Tutorial
April 21 | Amsterdam

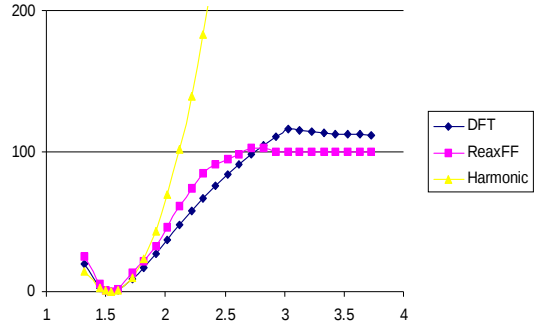
Outline

Molecular Dynamics Intro

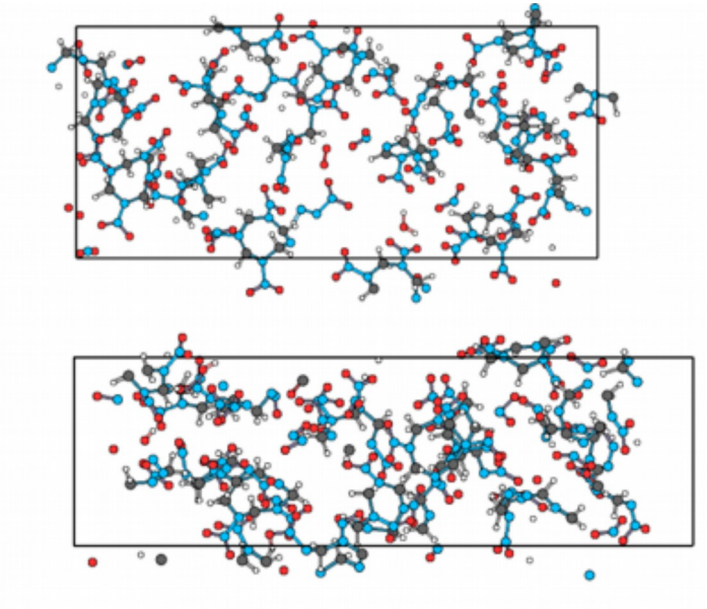


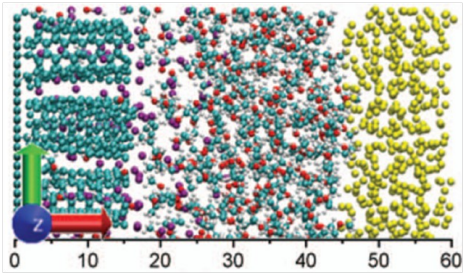
ReaxFF - general aspects

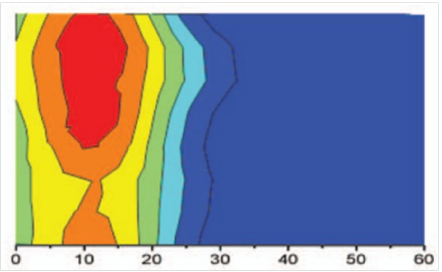


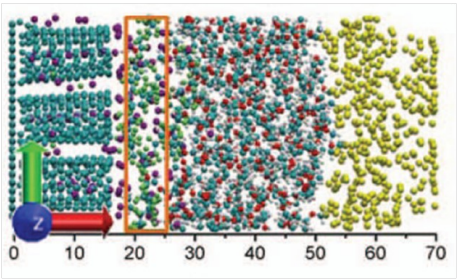


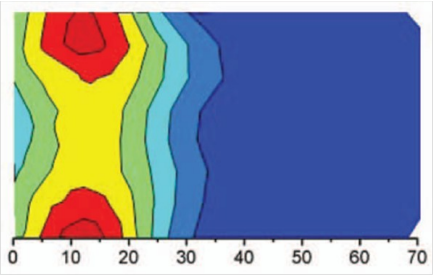
Selected ReaxFF studies











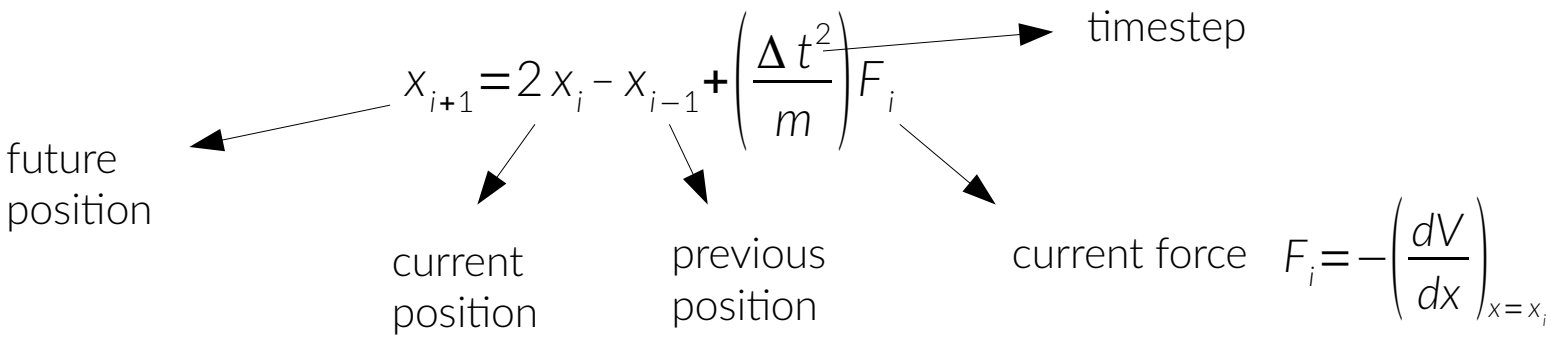
Molecular Dynamics (MD)

What?

Simulate physical movement of atoms and molecules.

How?

by numerically solving Newton's equation of motion, e.g. via the simple Verlet algorithm



Repeated application: positions and momenta as a function of time, x(t) p(t), termed the **Trajectory**.

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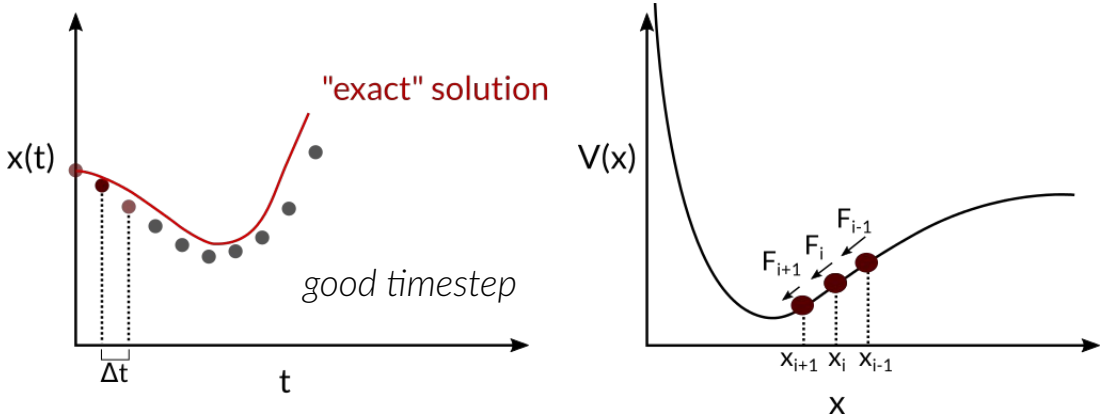
$$x_{i+1} = 2x_i - x_{i-1} + \left(\frac{\Delta t^2}{m}\right) F_i$$

- x_{i+1}: future position
- x_i: current position
- x_{i-1}: previous position
- Δt: timestep
- F_i: current force, $F_i = -\left(\frac{dV}{dx}\right)_{x=x_i}$

Repeated application: positions and momenta as a function of time, x(t) p(t), termed the **Trajectory**.

Important consequence:

Δt : discretization of time, from finite differences approach $\frac{dx}{dt} \approx \frac{\Delta x}{\Delta t}$



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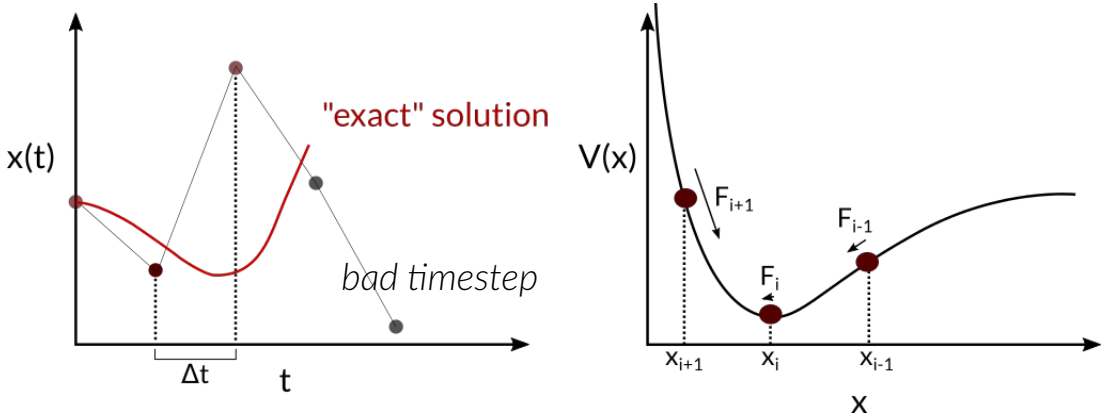


The length of Δt - and therefore t_{total} - is limited by the fastest movement in your system.

Typically: Δt ~ 1 fs

t_{total} ~ nanosecond(s)

Molecular Dynamics (MD)

What?

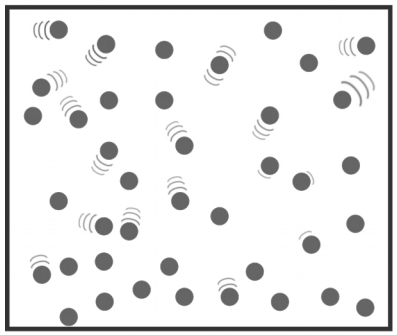
Simulate physical movement of atoms and molecules.

How?

by numerically solving Newton's equation of motion

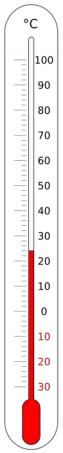
Why?

- conceptually simple and efficient (huge systems)
- study dynamic properties of systems, e.g. diffusion, etc...
- elegant link to macroscopic properties of materials
  through statistical mechanics/thermodynamics

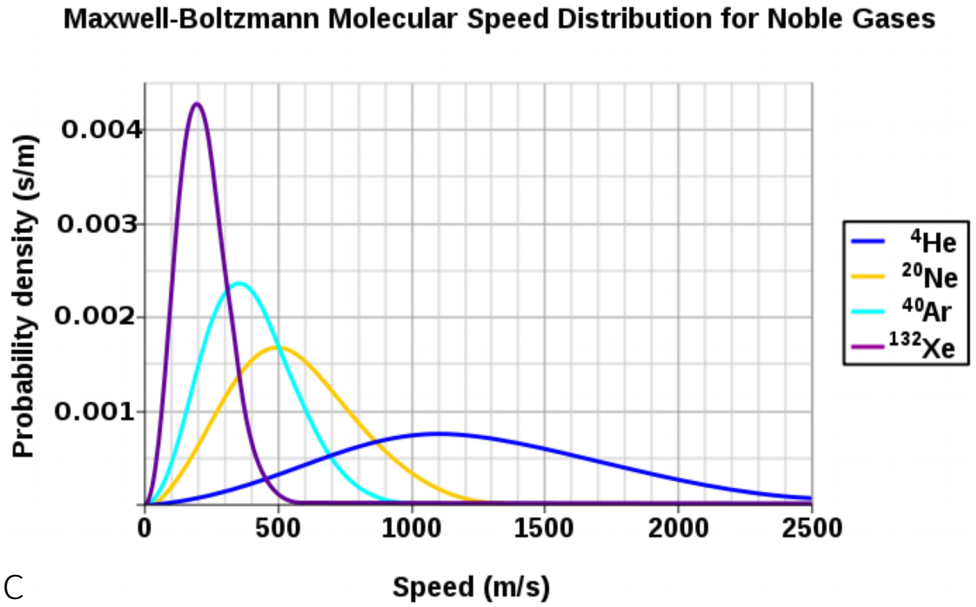


atomistic

linked



macroscopic



Source: https://en.wikipedia.org/wiki/Maxwell%E2%80%93Boltzmann_distribution

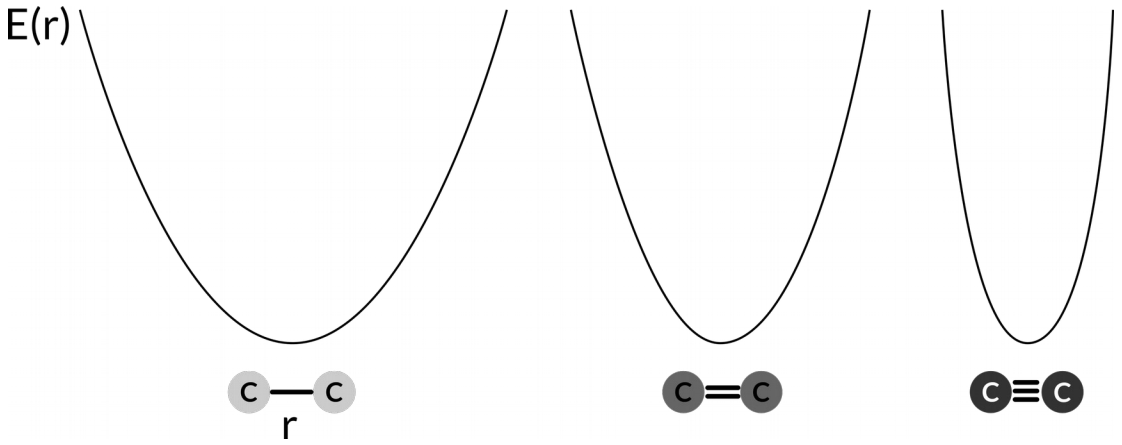
Force fields (FF)

MD requires forces: $F_i = -\left(\frac{dE}{dx}\right)_{x=x_i}$

Force fields:
E(x) for a given mol. structure via parametrized, analytic functions

$$E_{FF} = \underbrace{E_{bond} + E_{angle} + E_{dihedral}}_{\text{“bonded”}} + \underbrace{E_{electrostatic} + E_{v.d.Waals}}_{\text{“non-bonded”}}$$

Example: Harmonic potentials $E_{bond} = k\,(r-r_{eq.})^2$



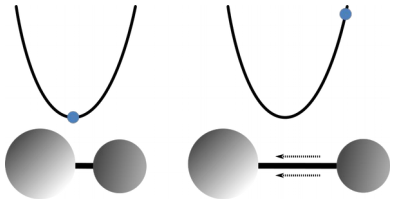
Parameters: k, r_{eq} per atomtype

Atomtypes: C ≠ C ≠ C

(CC_{single}, CC_{double}, CO_{single}, CO_{double}, etc…)

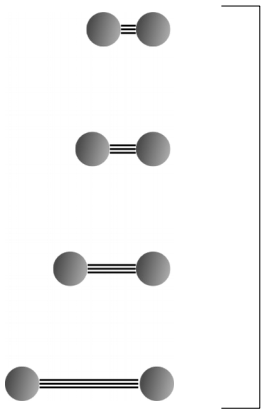
ReaxFF – The concept...

Standard forcefields vs *ReaxFF*



Fixed atomtypes and harmonic potentials:
bond breaking impossible, e.g.

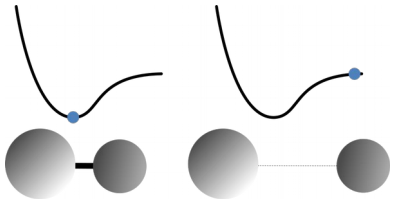
$E_{bond} \propto (distance)^2$



-a triple “bond” will always stay a triple “bond”

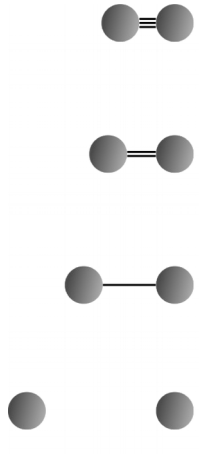
- a C_{triple} atom will always be a C_{triple} atom

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

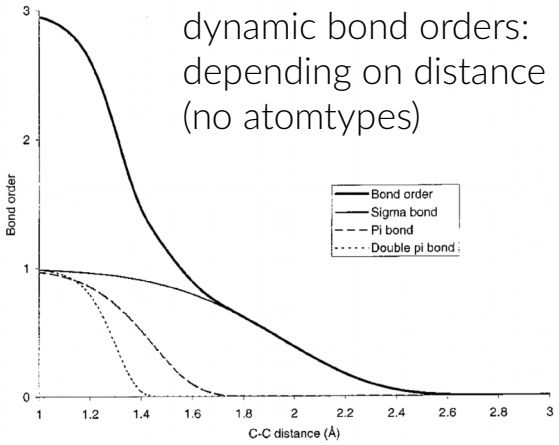


Non-harmonic potentials based on bond orders:
bond breaking/forming possible, e.g.

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



dynamic bond orders:
depending on distance
(no atomtypes)



($E_{bond} \rightarrow 0$)

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

ReaxFF – The concept…

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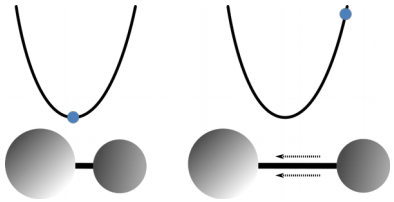

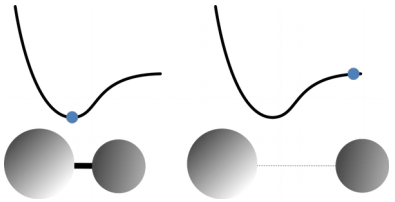

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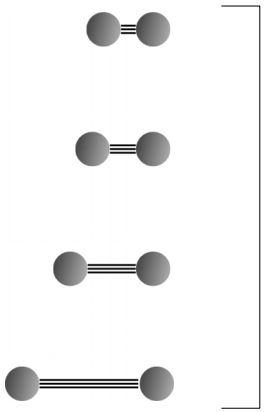

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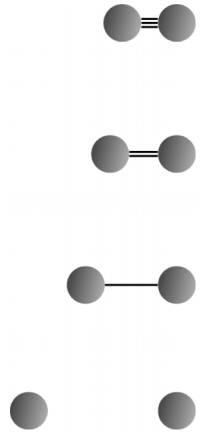

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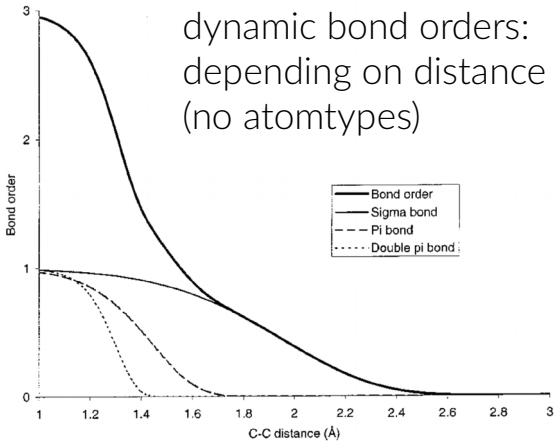

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Speed: (scaling) non-reactive MD (N^2) —~10-50 times faster→ **ReaxFF** (NlogN) —~1 000 000 times faster→ QM (conventional DFT) (N^3 or worse)

ReaxFF – Parameters

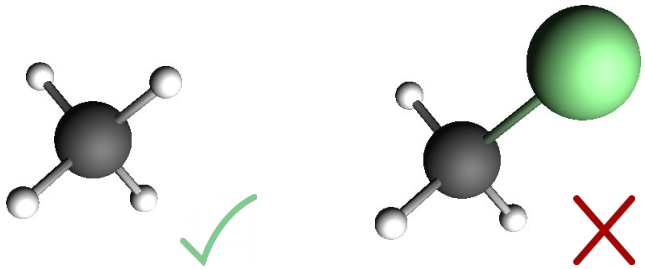
Parametersets included in ADF:

ADF 2013: 17 sets, 19 elements

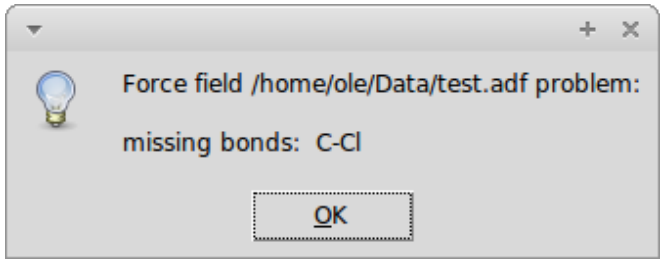
ADF 2014: 38 sets, 29 elements

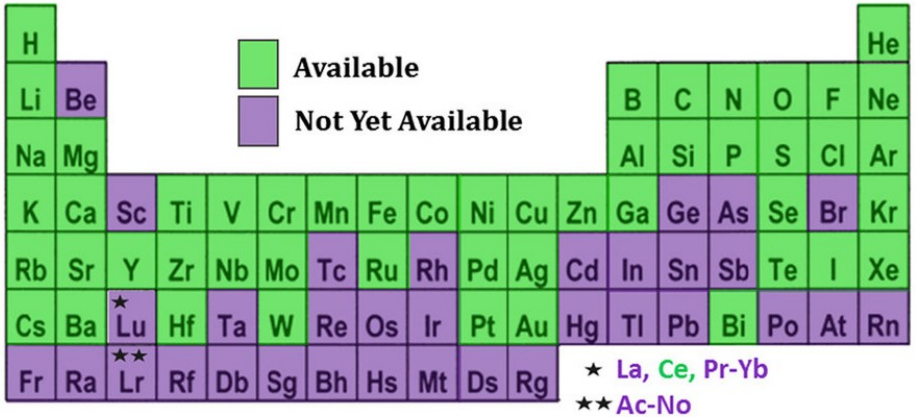
ADF 2016: 58 sets, 39 elements

Note:
Bonded terms for each pair are needed.
e. g. `FeOCHCl.ff`



CH_4 CH_3Cl





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

Sources for new ReaxFF parameters:

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

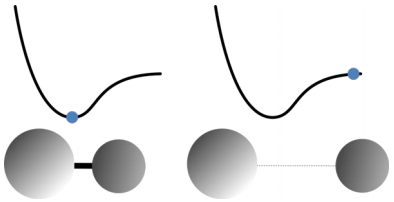
- RxFF_CONSULTING

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

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

ReaxFF

Concept



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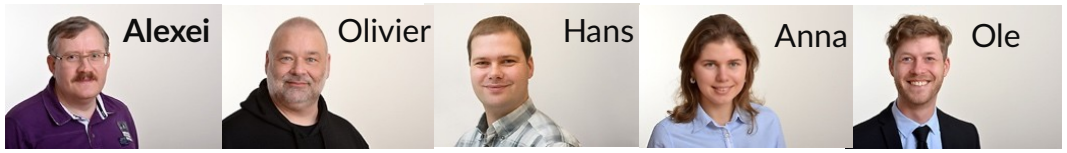
ReaxFF @ SCM

- *optimization & parallelization* of the original code.
- many parameters included (e.g. transition metals)
- GUI support
- automatic reaction event detection, rate constants
- analysis tools
- force-bias and grand canonical Monte Carlo
- internal parameter optimization via Monte Carlo



ReaxFF development

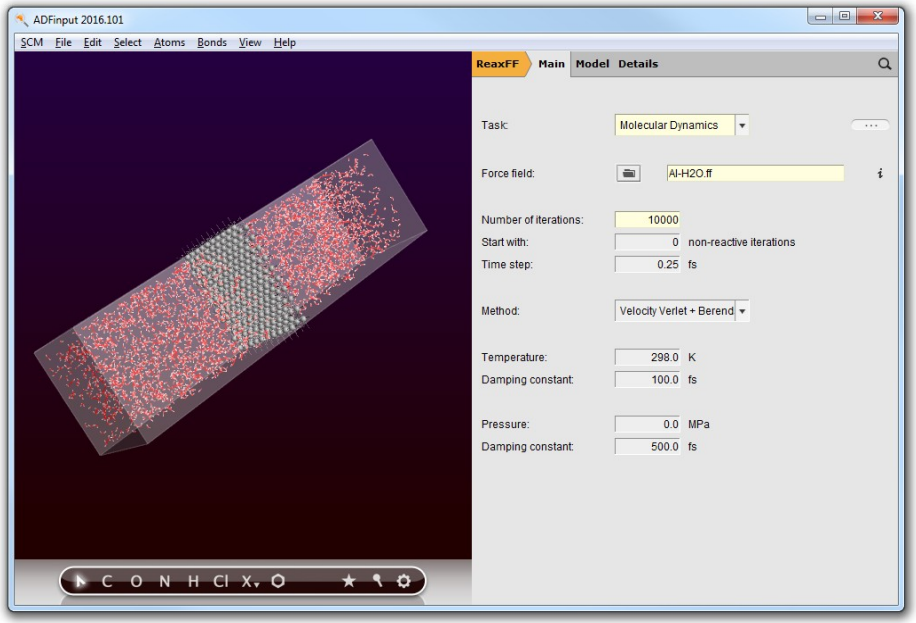
A.C.T. van Duin *et al*,*J. Phys. Chem. A* **2001**, 105, 9396-9409.

Adri

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

RxFF_CONSULTING

(ReaxFF-Parameters)



SCM

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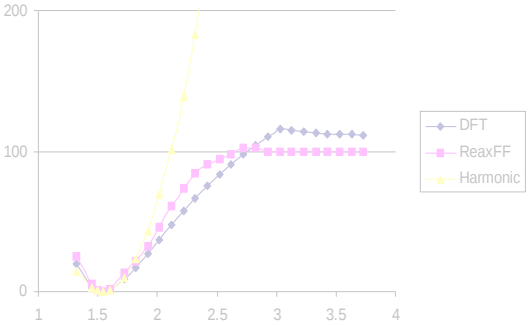

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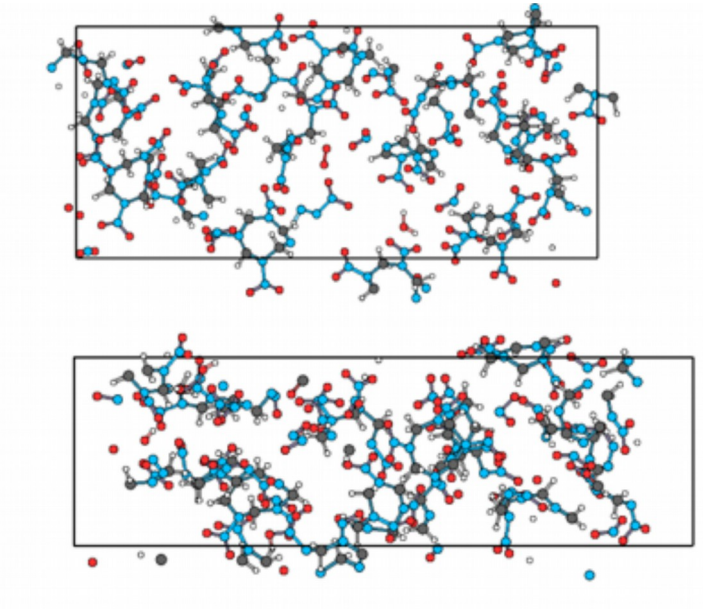
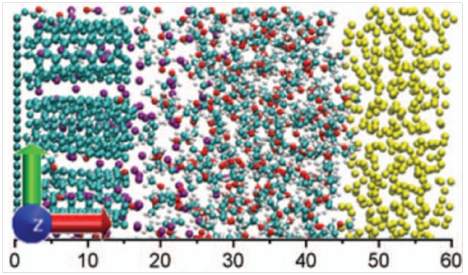
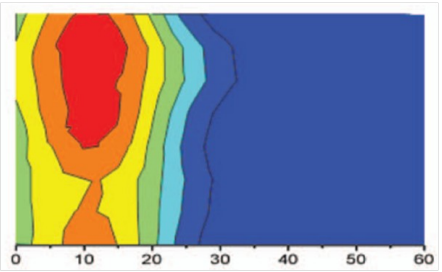
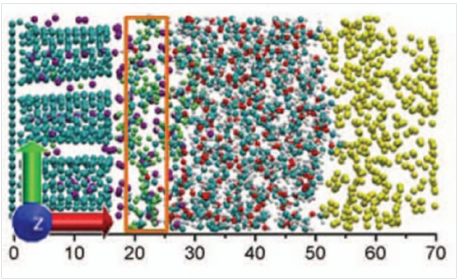
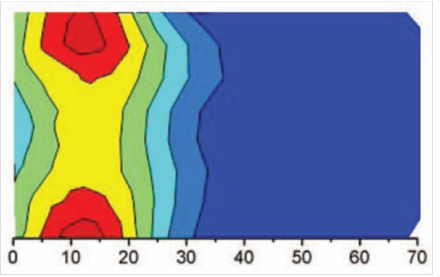




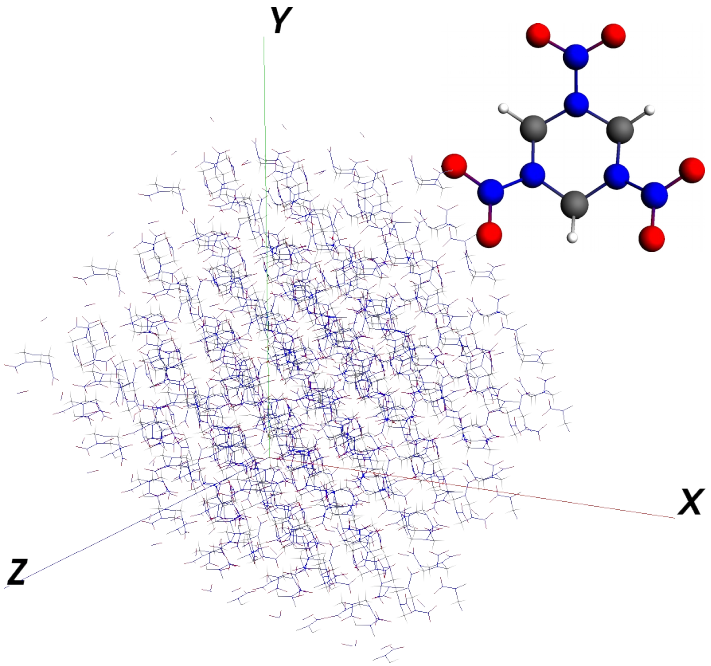






ReaxFF – Selected Research Highlights

L. Zhang , S. V. Zybin , A. C. T. Van Duin & W. A. Goddard III, *J. Energ. Mat.* **28,** 92–127 (*2010*).



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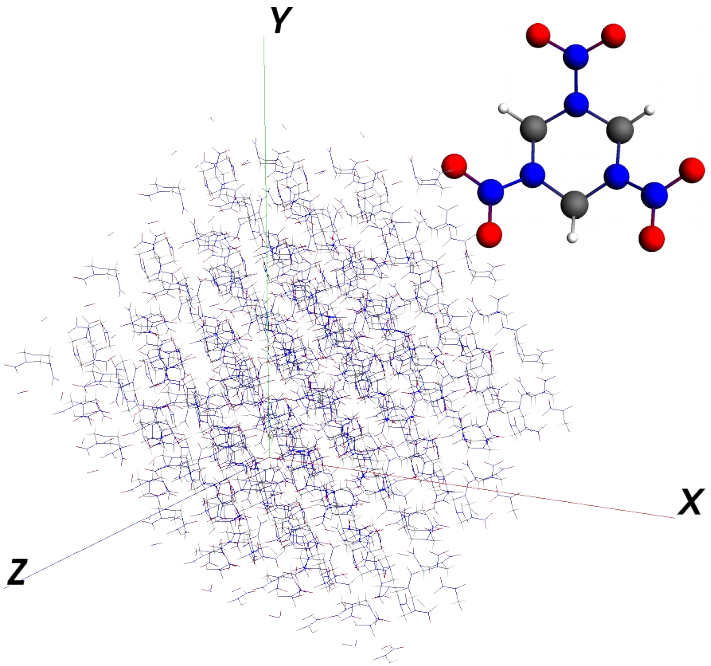

RDX: Research Department Formula X

- widely used commercial explosive
- approx. 1.5 x the explosive power of TNT
- very stable at ambient conditions

Simulate impact sensitivity?

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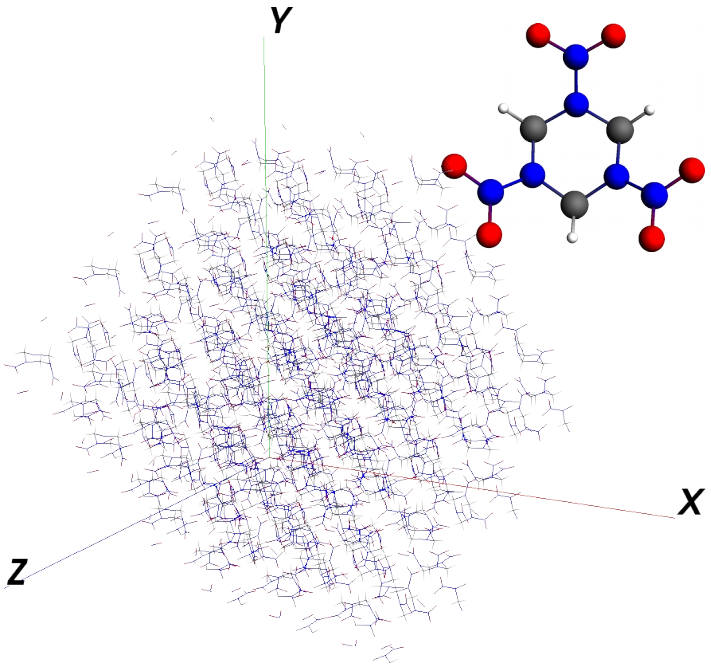

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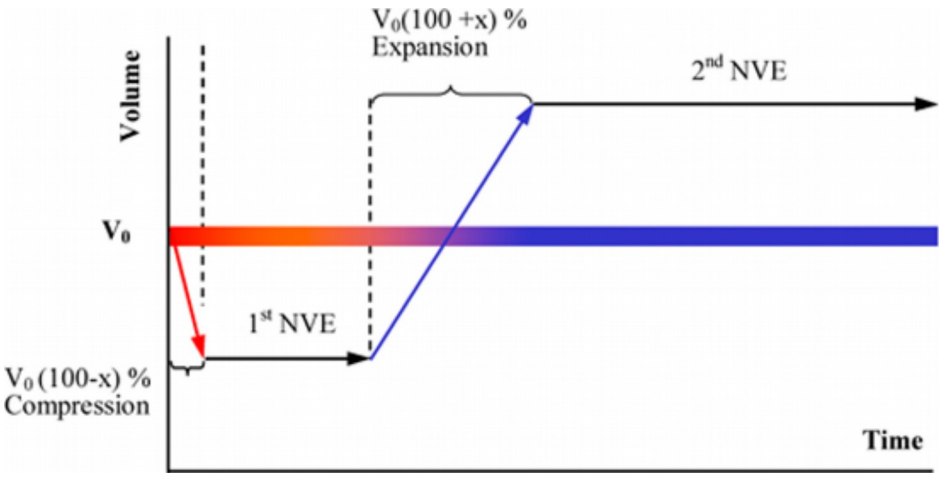
Simulate impact sensitivity!

Modeling of the high rate impact sensitivity



1. compression of volume
   (@ 8.76 km/s for 0.129 ps → (100-40)% V_0)
2. NVE dynamics for 1ps
3. expansion
   (@ 8.76 km/s for 0.862 ps → 140% V_0)
4. NVE dynamics for 4ps

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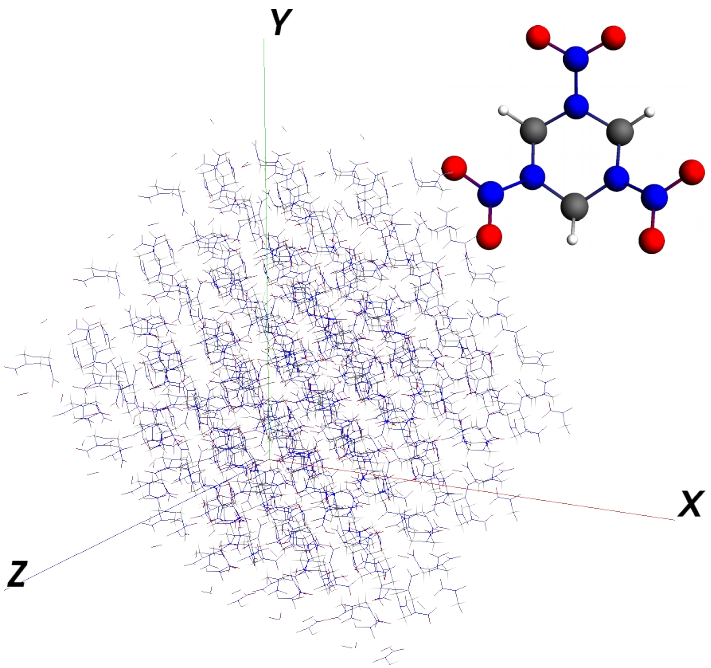

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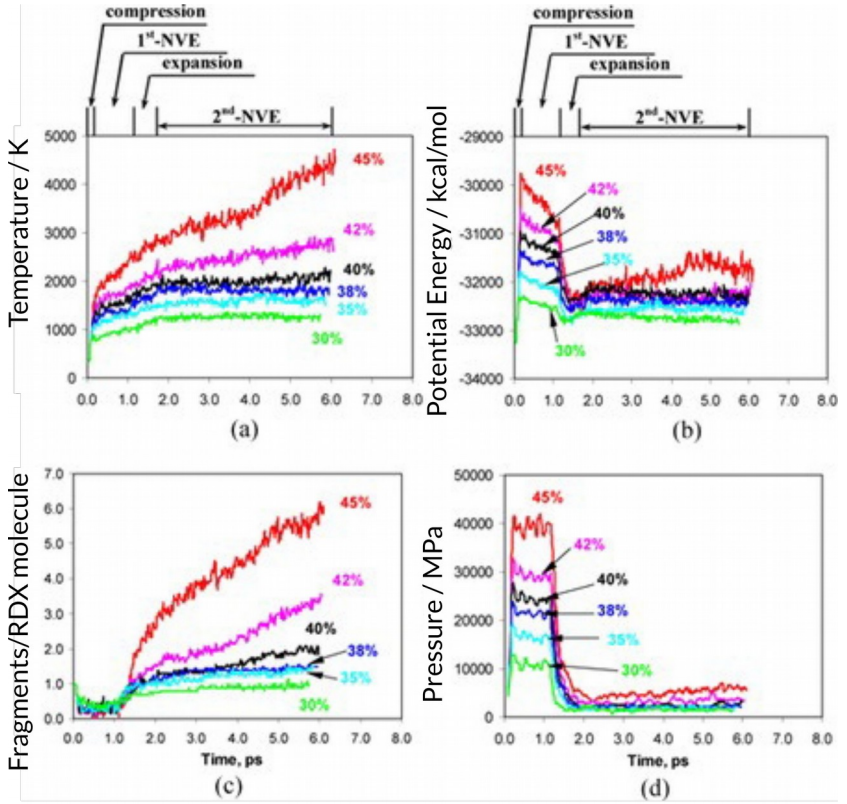


compression ratios in Volume @ 8.76 km/s

45%
42%
40%
38%
35%
30%

critical compression (BANG!)

ReaxFF – Selected Research Highlights

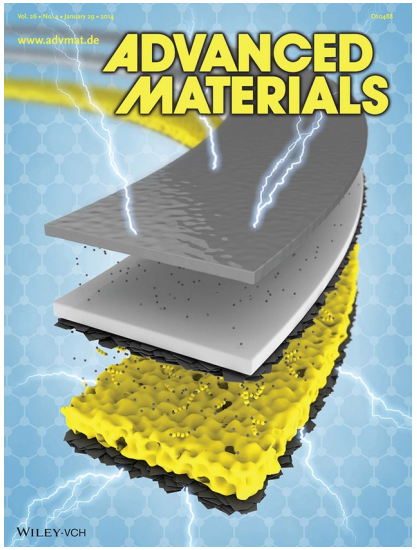
M. M. Islam, V. S. Bryantsev, and A. C. T. van Duin, *J. Electrochem. Soc.* **161**, *E3009-E3014* (2014).

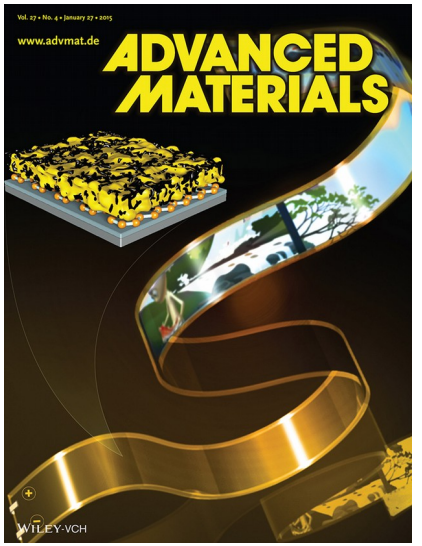
Lithium-Sulfur Batteries

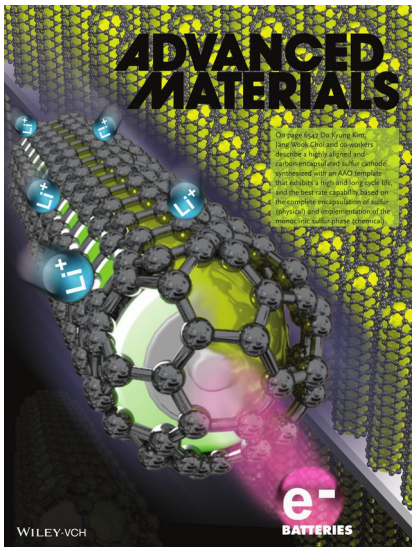
- high energy density
  (500 W·h/kg vs. 100-250 W·h/kg in Li-ion)
- environmental friendliness
- abundance and lowcost

Problems

- unwanted reactions between Li and electrolyte
- during charging Li can deposit as metallic phase on the anode surface
- dissolved polysulfides anions migrate through electrolyte → insoluble sulfides passivate the anode…
- …







ReaxFF – Selected Research Highlights

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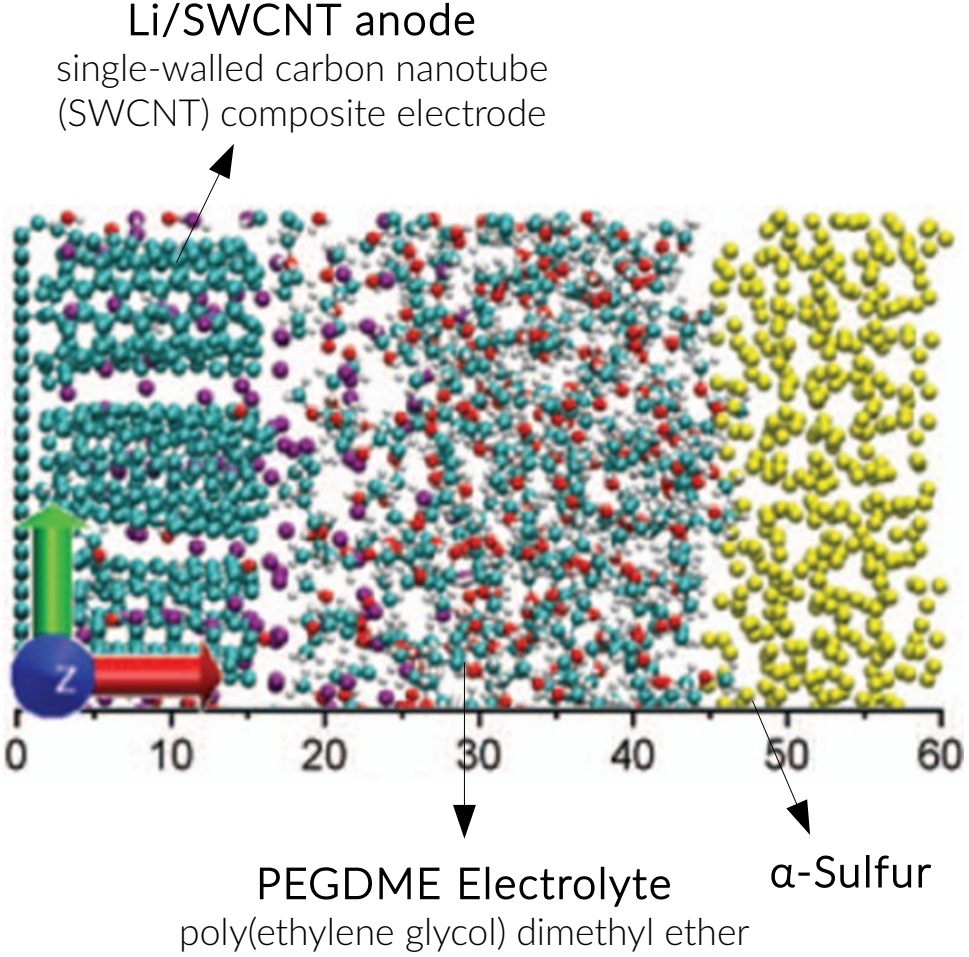
Modeling with ReaxFF:



NVT-MD simulations at 300 K

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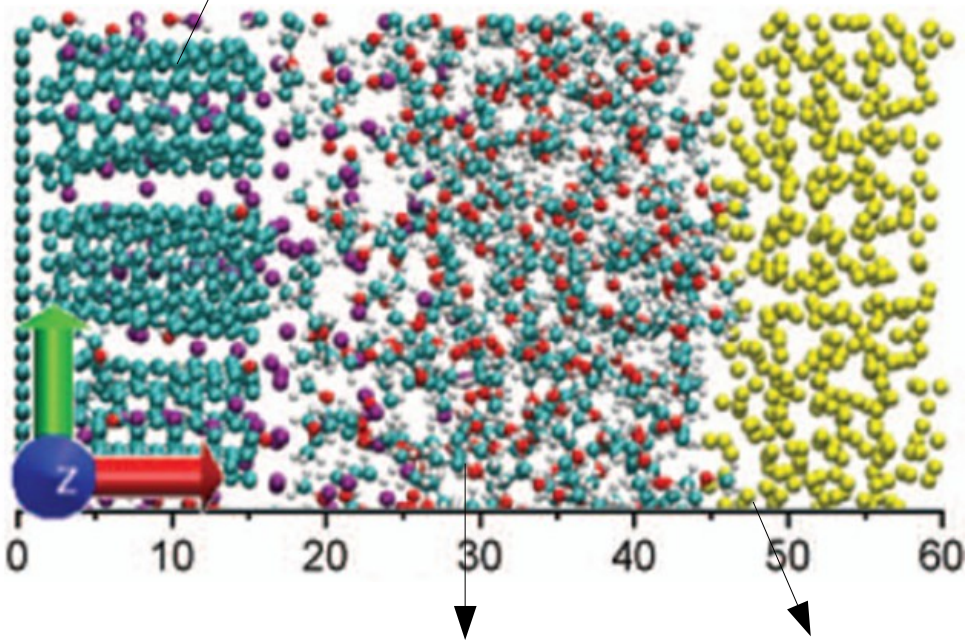
Lithium-Sulfur Batteries modeling with ReaxFF:

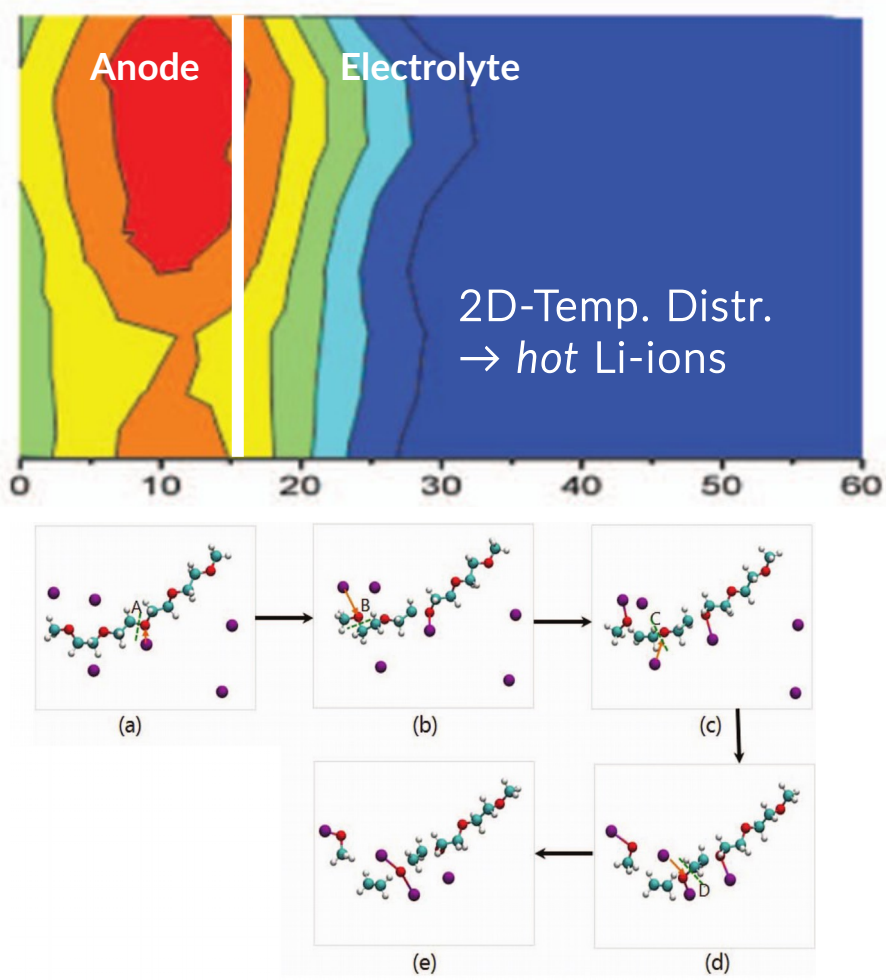
Li/SWCNT anode
single-walled carbon nanotube (SWCNT) composite electrode



PEGDME Electrolyte
poly(ethylene glycol) dimethyl ether

α-Sulfur

NVT-MD simulations at 300 K



Electrolyte dissociation, build up of ethylene

ReaxFF – Selected Research Highlights

M. M. Islam, V. S. Bryantsev, and A. C. T. van Duin, *J. Electrochem. Soc.* **161**, *E3009-E3014* (2014).

Lithium-Sulfur Batteries modeling with ReaxFF:

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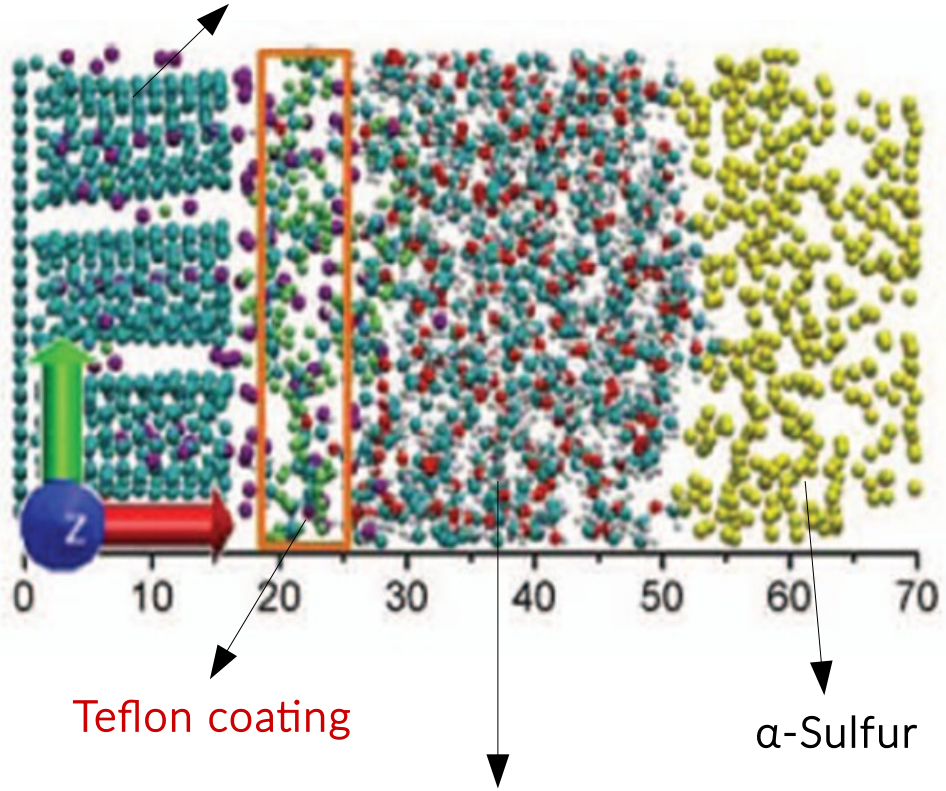
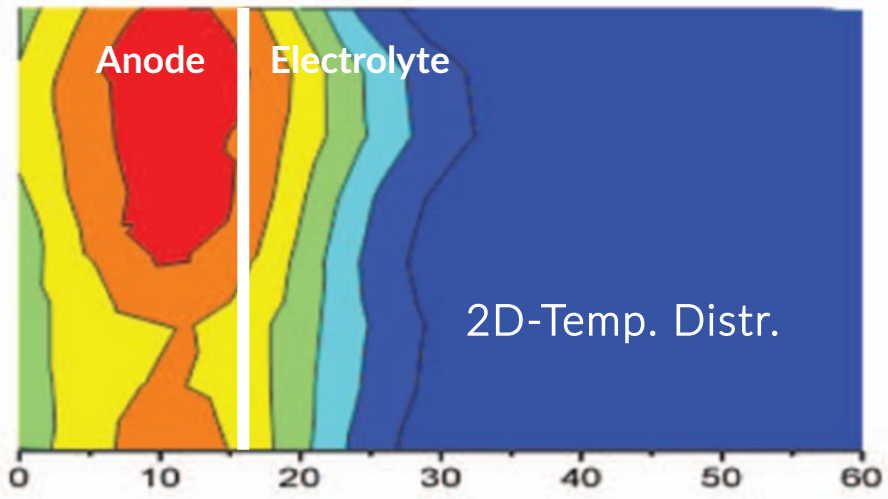
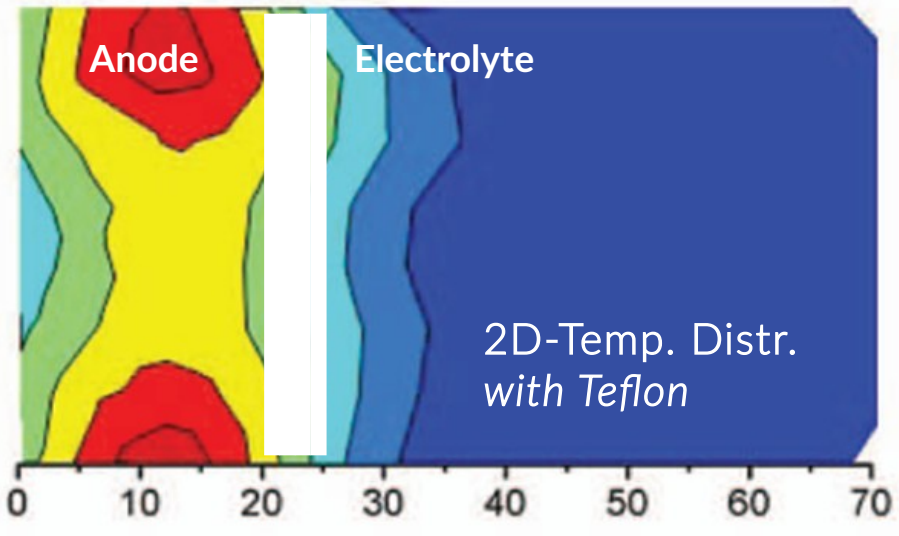


Teflon coating

α-Sulfur

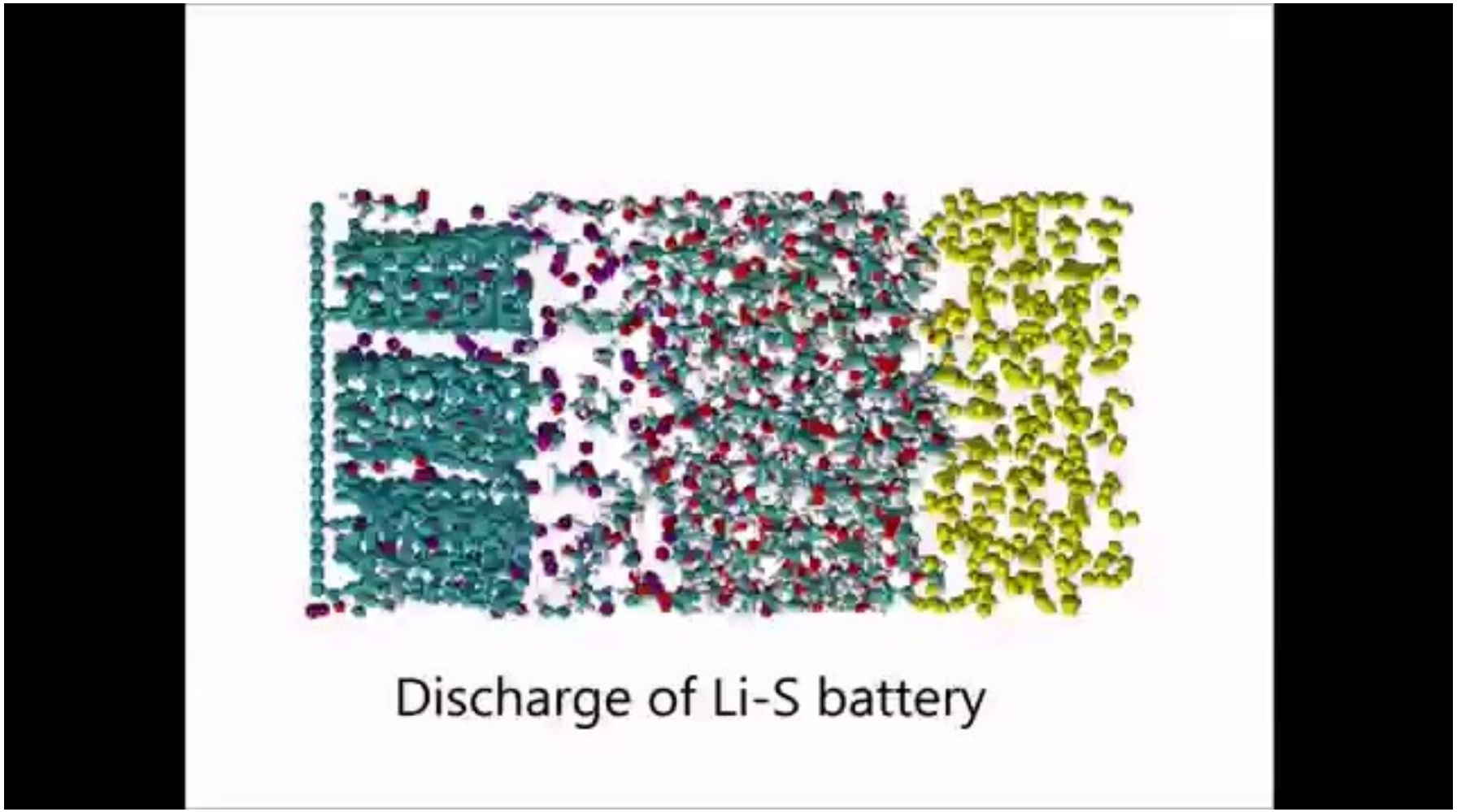
PEGDME Electrolyte
poly(ethylene glycol) dimethyl ether





Electrolyte is protected, ethylene reduced by 90%

ReaxFF – Research Highlights



https://www.youtube.com/watch?v=frDmCf1zzYg

The End.

-contact-

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

Appendix

Inside ReaxFF – Parameters

Example: Bond orders from atom distance…

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

In: distance between atoms, r_{ij}

Out: 1, 2, 1.42, etc…

Parameters = 9

$p_{bo,1}$,$p_{bo,2}$,$p_{bo,3}$,$p_{bo,4}$,$p_{bo,5}$,$p_{bo,6}$,r_0, $r_{0,\pi}$, $r_{0,\pi\pi}$

Inside ReaxFF – Parameters

Example: Bond orders from atom distance…

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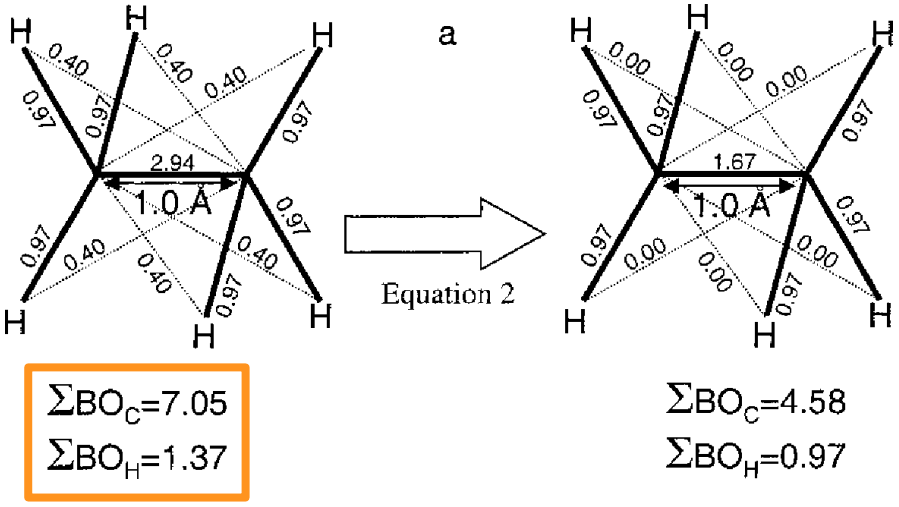
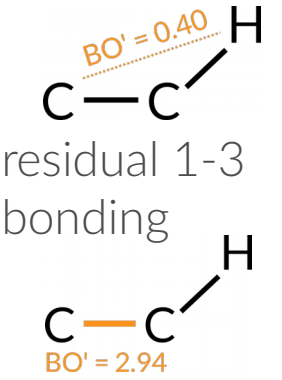
Out: 1, 2, 1.42, etc…

Parameters = 9

$p_{bo,1}, p_{bo,2}, p_{bo,3}, p_{bo,4}, p_{bo,5}, p_{bo,6}, r_0, r_{0,\pi}, r_{0,\pi\pi}$

Problems: Resulting bond orders not correct…





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

Inside ReaxFF – Parameters

Example term: Bond orders from atom distance…

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

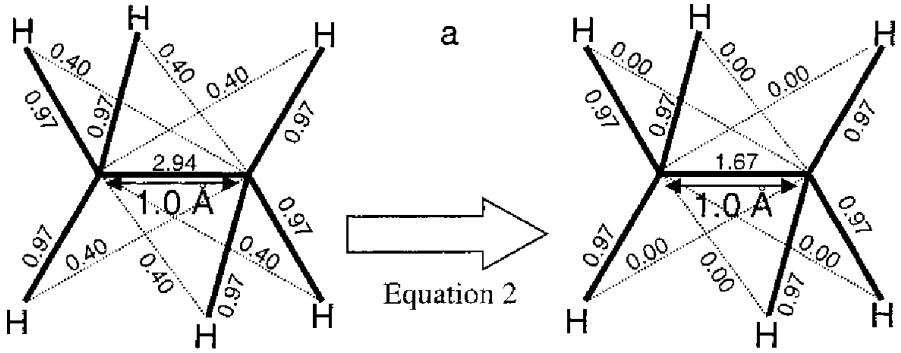
In: distance between atoms, r_{ij}

Out: 1, 2, 1.42, etc…

Parameters = 16

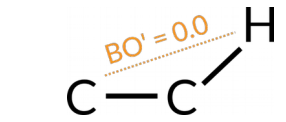
$p_{bo,1}$,$p_{bo,2}$,$p_{bo,3}$,$p_{bo,4}$,$p_{bo,5}$,$p_{bo,6}$,r_0, $r_{0,\pi}$, $r_{0,\pi\pi}$
val_1, val_2, λ_1,λ_2,λ_3,λ_4,λ_5

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

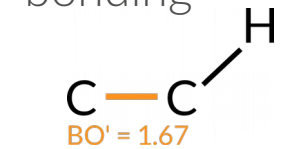


ΣBO_C=7.05
ΣBO_H=1.37

ΣBO_C=4.58
ΣBO_H=0.97



~~residual 1-3 bonding~~



~~overbonding~~

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

Inside ReaxFF – Parameters

Example term: Bond orders from atom distance…

`CHO.ff:`

Reactive MD-force field c/h/o combustion force field:
Chenoweth, K.; van Duin, A.C.T.; Goddard, W.A.
J. Phys. Chem. A 2008, 112, 1040-1053.
39 ! Number of general parameters
50.0000 !p(boc1)
9.5469 !p(boc2)
26.5405 !p(coa2)
1.5105 !p(trip4)
[…SNIP…]
3 ! Nr of atoms; atomID;ro(sigma); Val;atom mass;Rvdw;Dij;gamma;ro(pi);Val(e)
alfa;gamma(w);Val(angle);p(ovun5);n.u.;chiEEM;etaEEM;n.u.
ro(pipi);p(lp2);Heat increment;p(boc4);p(boc3);p(boc5),n.u.;n.u.
p(ovun2);p(val3);n.u.;Val(boc);p(val5);n.u.;n.u.;n.u.
C 1.3825 4.0000 12.0000 1.9133 0.1853 0.9000 1.1359 4.0000
9.7602 2.1346 4.0000 33.2433 79.5548 5.8678 7.0000 0.0000
1.2104 0.0000 199.0303 8.6991 34.7289 13.3894 0.8563 0.0000
-2.8983 2.5000 1.0564 4.0000 2.9663 0.0000 0.0000 0.0000
H 0.7853 1.0000 1.0080 1.5904 0.0419 1.0206 -0.1000 1.0000
[…SNIP…]
6 ! Nr of bonds; at1;at2;De(sigma);De(pi);De(pipi);p(be1);p(bo5);13corr;n.u.;p(bo6),p(ovun1)
p(be2);p(bo3);p(bo4);n.u.;p(bo1);p(bo2)
1 1 156.5953 100.0397 80.0000 -0.8157 -0.4591 1.0000 37.7369 0.4235
[…SNIP…]

BO-Parameters: 16

$p_{bo,1}$,$p_{bo,2}$,$p_{bo,3}$,$p_{bo,4}$,$p_{bo,5}$,$p_{bo,6}$, r_0, $r_{0,\pi}$, $r_{0,\pi\pi}$
val_1, val_2, λ_1,λ_2,λ_3,λ_4,λ_5