Using the ReaxFF program

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Contents

- ReaxFF energy terms
- ReaxFF program structure
- Overview ReaxFF in- and output files
    - General
    - MD-simulations
    - Energy minimization
- Examples:
    - Single molecules: minimization, MD, cookoff
    - Periodic molecular systems: building, compression, cookoff and piston simulations
    - Combined molecular/condensed systems: building and MD
- Additional ReaxFF features
        - Multiple thermostats
        - Cell volume manipulation
        - Electric field
        - Bond, angle and torsion restraints
        - Introduction of new molecules during MD-simulation
    - Force field development

ReaxFF energy terms

$$E_{system} = E_{bond} + E_{lp} + E_{over} + E_{under} + E_{val} + E_{pen} + E_{coa} + E_{C2}$$
$$+ E_{tors} + E_{conj} + E_{H-bond} + E_{vdWaals} + E_{Coulomb}$$

- E_{bond}: bond energy; attractive term, directly derived from bond orders
- E_{lp}: Lone pair energy; penalty for breaking up lone pairs in O, N
- E_{over}: Overcoordination energy: penalty for overcoordinating atoms
- E_{under}: Undercoordination energy: stabilizes undercoordinated atoms
- E_{val}: Angle strain; equilibrium angle depends on bond order central atom
- E_{pen}: Penalty for 'allene'-type molecules ($H_2C=C=CH_2$)
- E_{coa}: Angle conjugation; stabilizes $-NO_2$ groups
- E_{C2}: C_2 correction: destabilizes C=C
- E_{tors}: Torsion energy: bond-order dependent V_2-term
- E_{conj}: Torsion conjugation: general conjugation stability
- $E_{H\text{-}bond}$: Hydrogen bond
- $E_{vdWaals}$: van der Waals: calculated between every atom
- $E_{Coulomb}$: Coulomb interaction: calculated between every atom; polarizable charges get updated every iteration

General

Special case

ReaxFF general energy terms

$$E_{system} = E_{bond} + E_{over} + E_{val} + E_{tors} + E_{vdWaals} + E_{Coulomb}$$ Covalent materials

- E_{bond}: bond energy; attractive term, directly derived from bond orders
- E_{over}: Overcoordination energy: penalty for overcoordinating atoms
- E_{val}: Angle strain; equilibrium angle depends on bond order central atom
- E_{tors}: Torsion energy: bond-order dependent V_2-term
- $E_{vdWaals}$: van der Waals: calculated between every atom
- $E_{Coulomb}$: Coulomb interaction: calculated between every atom

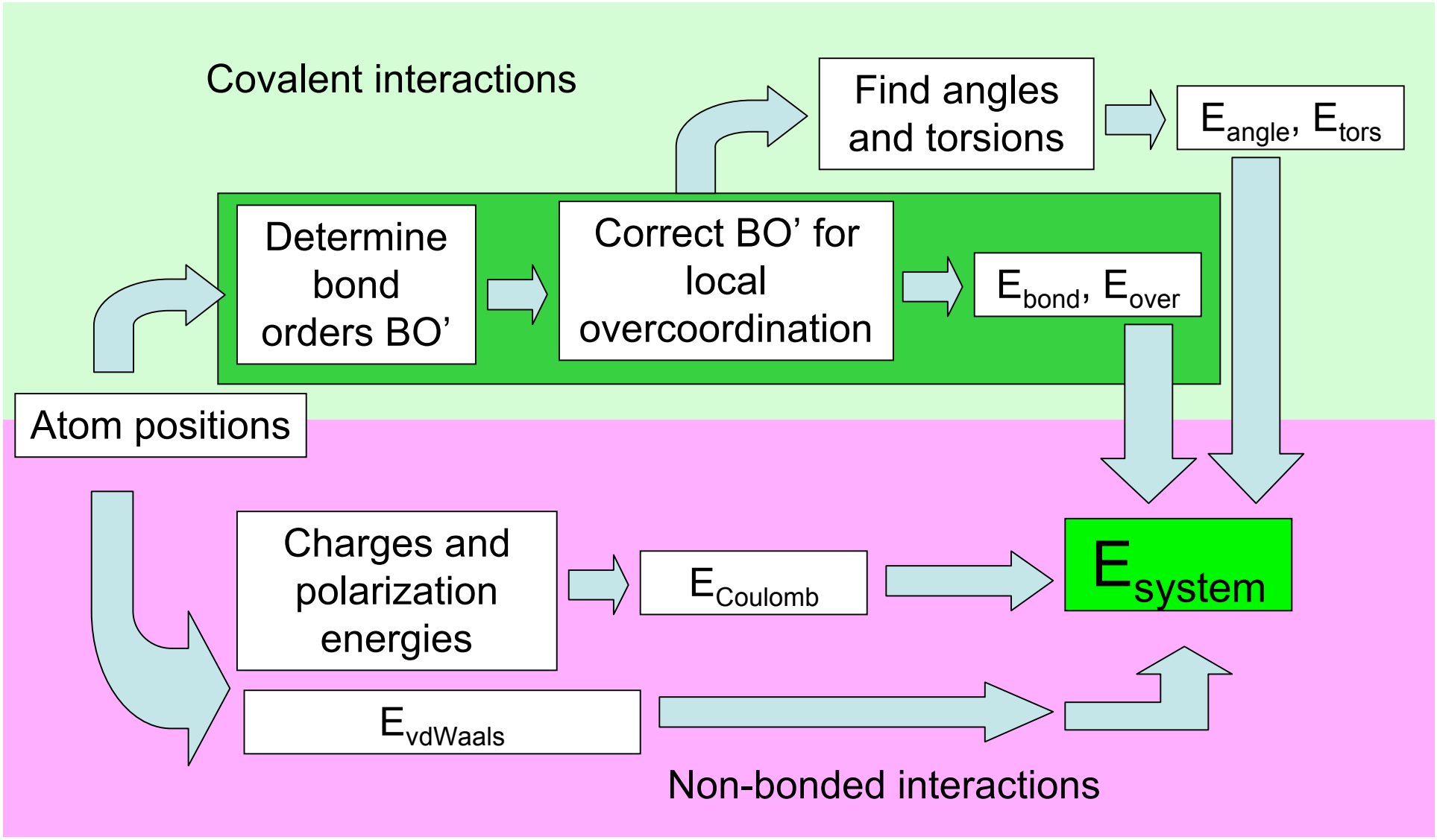
$$E_{system} = E_{bond} + E_{over} + E_{vdWaals} + E_{Coulomb}$$ Metal alloys

$$E_{system} = E_{bond} + E_{over} + E_{vdWaals}$$ Metals

$$E_{system} = E_{vdWaals} + E_{Coulomb}$$ Ionic materials

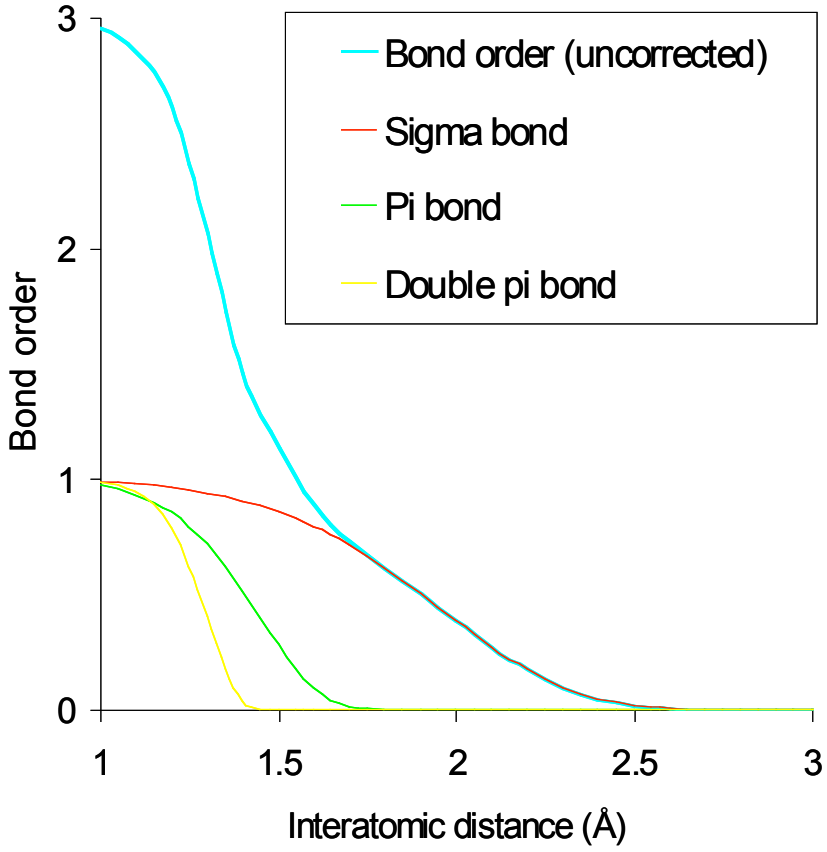
$$E_{system} = E_{vdWaals}$$ Noble gases

ReaxFF flow diagram



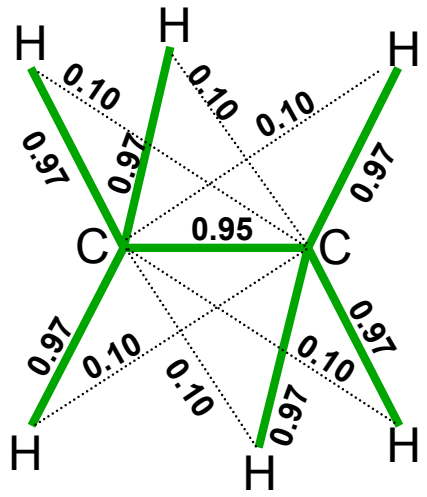
Calculation of bond orders from interatomic distances

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



Bond order correction

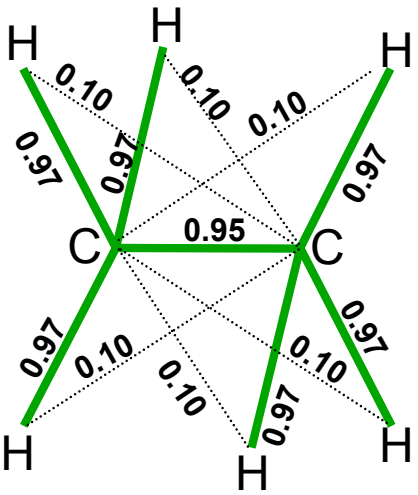
Uncorrected bond orders in ethane

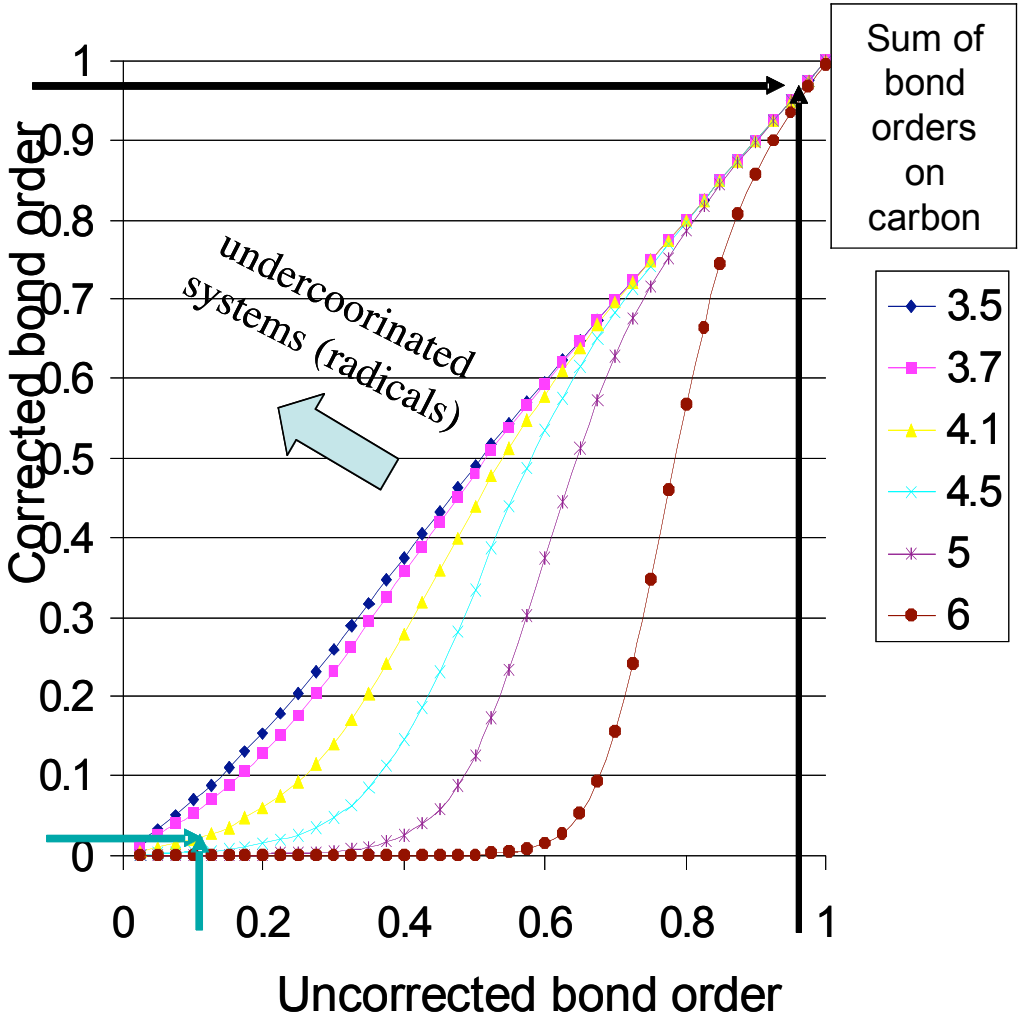


$\Sigma BO_C = 4.16$

$\Sigma BO_H = 1.17$

- Unphysical; normally coordinated atoms should not have binding interactions with next-neighbours
- Puts strain on angle and overcoordination potentials
- Short-range bond orders will not capture transition states





Corrected bond orders

Uncorrected bond orders

$$BO_{ij}^{\sigma} = BO_{ij}^{'\sigma} \cdot f_1(\Delta_i^{'},\Delta_j^{'}) \cdot f_4(\Delta_i^{'},BO_{ij}^{'}) \cdot f_5(\Delta_j^{'},BO_{ij}^{'})$$

$$BO_{ij}^{\pi} = BO_{ij}^{'\pi} \cdot f_1(\Delta_i^{'},\Delta_j^{'}) \cdot f_1(\Delta_i^{'},\Delta_j^{'}) \cdot f_4(\Delta_i^{'},BO_{ij}^{'}) \cdot f_5(\Delta_j^{'},BO_{ij}^{'})$$

$$BO_{ij}^{\pi\pi} = BO_{ij}^{'\pi\pi} \cdot f_1(\Delta_i^{'},\Delta_j^{'}) \cdot f_1(\Delta_i^{'},\Delta_j^{'}) \cdot f_4(\Delta_i^{'},BO_{ij}^{'}) \cdot f_5(\Delta_j^{'},BO_{ij}^{'})$$

$$BO_{ij} = BO_{ij}^{\sigma} + BO_{ij}^{\pi} + BO_{ij}^{\pi\pi}$$

$$\Delta_i^{'boc} = -Val_i^{boc} + \sum_{j=1}^{neighbours(i)} BO_{ij}^{'}$$

$$f_1(\Delta_i,\Delta_j) = \frac{1}{2} \cdot \left(\frac{Val_i + f_2(\Delta_i^{'},\Delta_j^{'})}{Val_i + f_2(\Delta_i^{'},\Delta_j^{'}) + f_3(\Delta_i^{'},\Delta_j^{'})} + \frac{Val_j + f_2(\Delta_i^{'},\Delta_j^{'})}{Val_j + f_2(\Delta_i^{'},\Delta_j^{'}) + f_3(\Delta_i^{'},\Delta_j^{'})} \right)$$

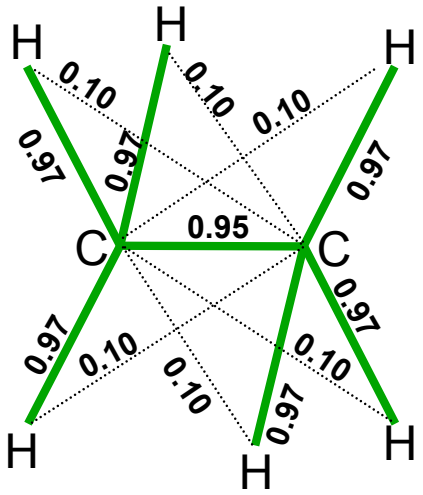
$$f_2(\Delta_i^{'},\Delta_j^{'}) = \exp(-p_{boc1} \cdot \Delta_i^{'}) + \exp(-p_{boc1} \cdot \Delta_j^{'})$$

$$f_3(\Delta_i^{'},\Delta_j^{'}) = -\frac{1}{p_{boc2}} \cdot \ln\left\{ \frac{1}{2} \cdot \left[\exp\left(-p_{boc2} \cdot \Delta_i^{'}\right) + \exp\left(-p_{boc2} \cdot \Delta_j^{'}\right) \right] \right\}$$

$$f_4(\Delta_i^{'},BO_{ij}^{'}) = \frac{1}{1 + \exp(-p_{boc3} \cdot (p_{boc4} \cdot BO_{ij}^{'} \cdot BO_{ij}^{'} - \Delta_i^{'boc}) + p_{boc5})}$$

- Normally coordinated carbon will not make weak bonds, under-coordinated carbon (radical) can make weak bonds (no correction)

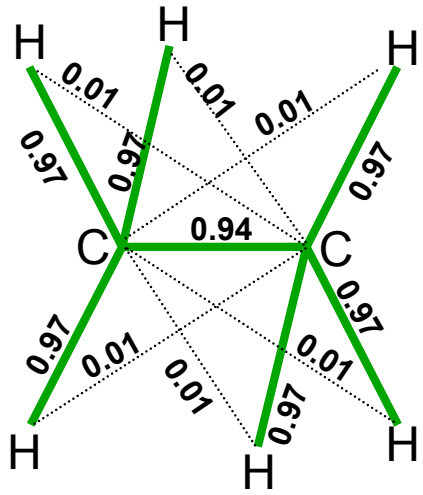
Uncorrected bond orders



$\Sigma BO_C = 4.16$

$\Sigma BO_H = 1.17$

Corrected bond orders



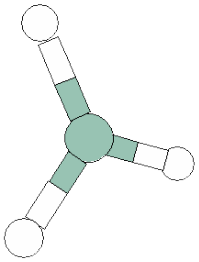
$\Sigma BO_C = 3.88$

$\Sigma BO_H = 0.98$

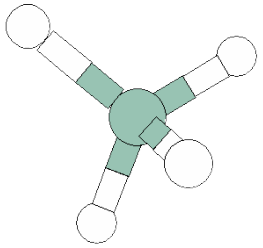
- Correction removes unrealistic weak bonds but leaves strong bonds intact
- Increases computational expense as bond orders become multibody interactions
- Correction only applied for covalent-systems, not for metals

Overcoordination

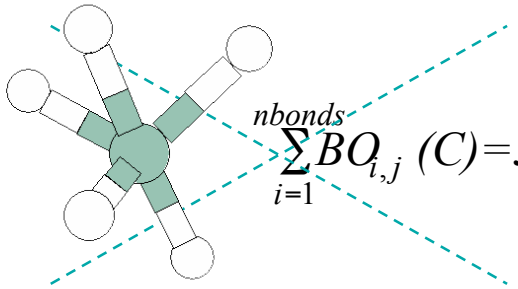
Avoid unrealistically high amounts of bond orders on atoms



$$\sum_{i=1}^{nbonds} BO_{i,j}\,(C)=3$$



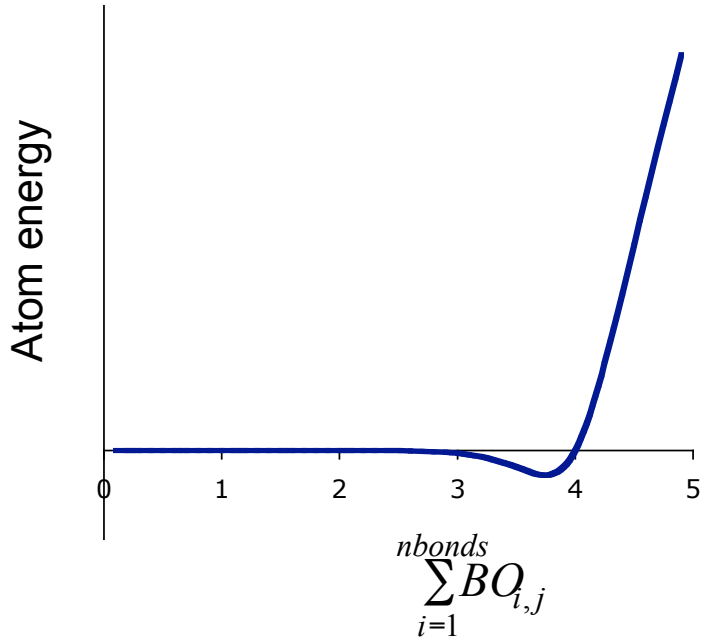
$$\sum_{i=1}^{nbonds} BO_{i,j}\,(C)=4$$



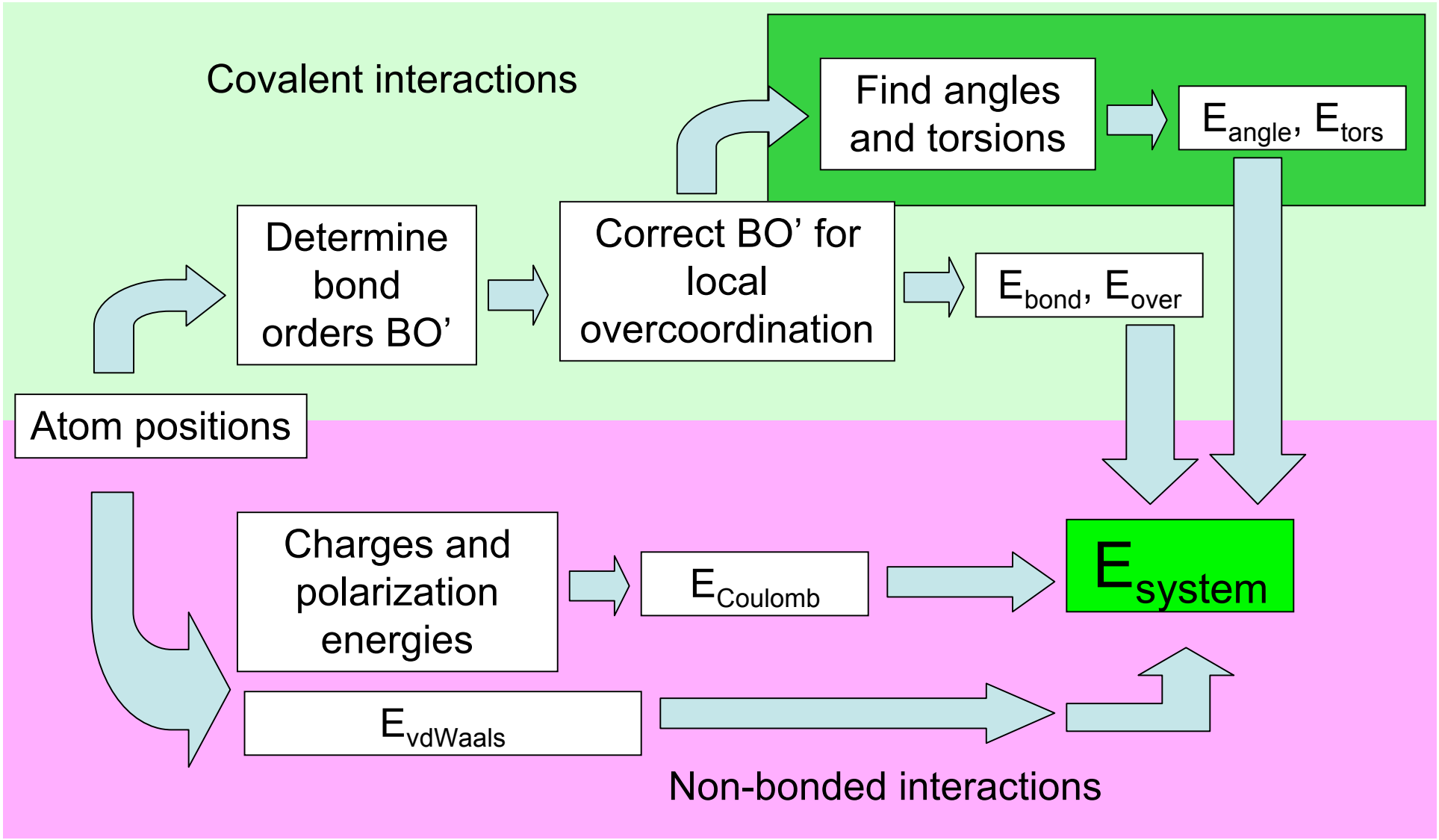
$$\sum_{i=1}^{nbonds} BO_{i,j}\,(C)=5$$

$$E_{over} = f(BO_{ij}) \cdot \Delta_i \cdot \frac{1}{1+\exp(\lambda \cdot \Delta_i)}$$

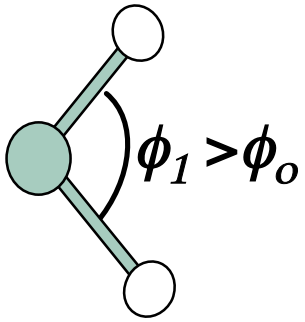
$$\Delta_i = Valency_i - \sum_{j=1}^{neighbours} BO_{ij}$$



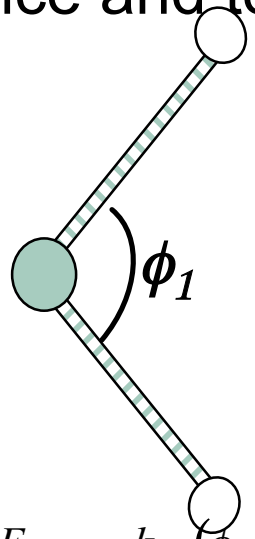
ReaxFF flow diagram



Valence and torsion angles

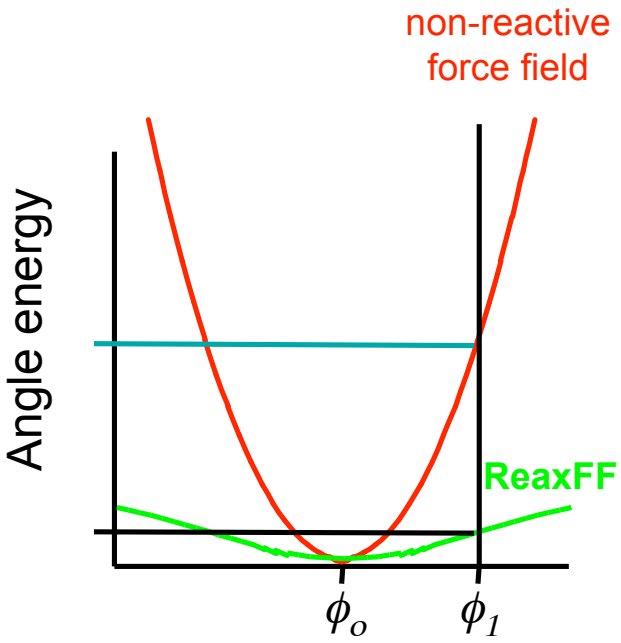


Bond orders: 1



$E_{angle} = k_a \cdot (\phi - \phi_o)^2$

Bond orders: 0.4



Non-reactive: $E_{angle} = k_a \cdot (\phi - \phi_o)^2$

Reactive: $E_{angle} = \left[1 - \exp\left(\lambda_3 \cdot BO_a^3\right)\right]\left[1 - \exp\left(\lambda_3 \cdot BO_b^3\right)\right]\left\{k_a - k_a \exp\left[-k_b \cdot (\phi - \phi_o)^2\right]\right\}$

Bond-order dependent part

- Equilibrium angle is bond-order dependent
- Stronger pi-bond character increases equilbrium angle

$$\phi_0(BO) = \pi - \phi_{0,0} \cdot \left\{1 - \exp\left[-p_{val10} \cdot \left(2 - f(BO_\pi)\right)\right]\right\}$$

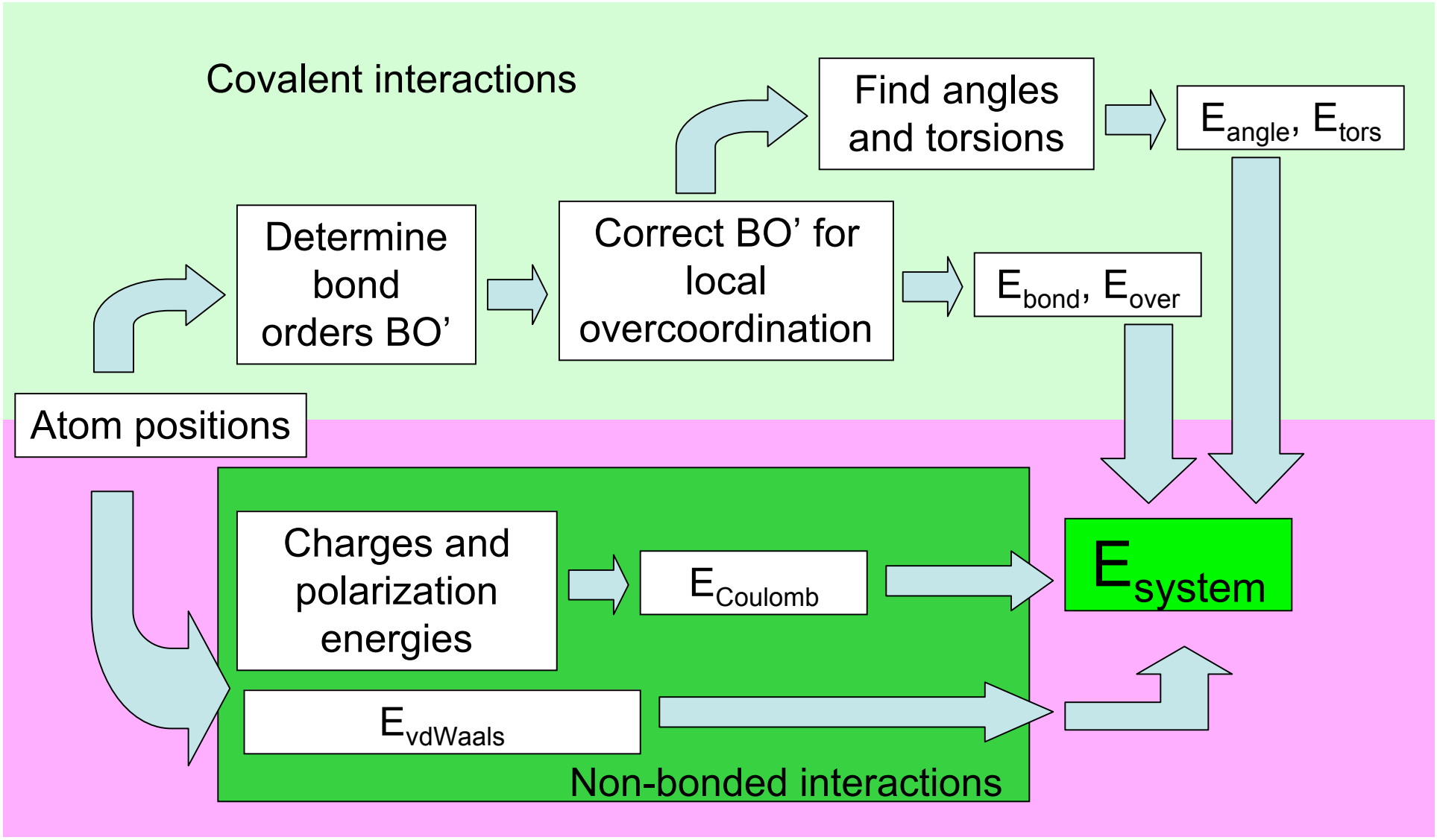
BO_a = Bond order a

BO_b = Bond order b

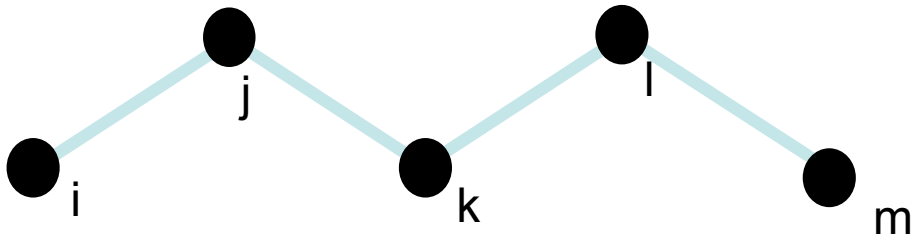
ϕ = Angle

ϕ_o = Equilibrium angle

ReaxFF flow diagram



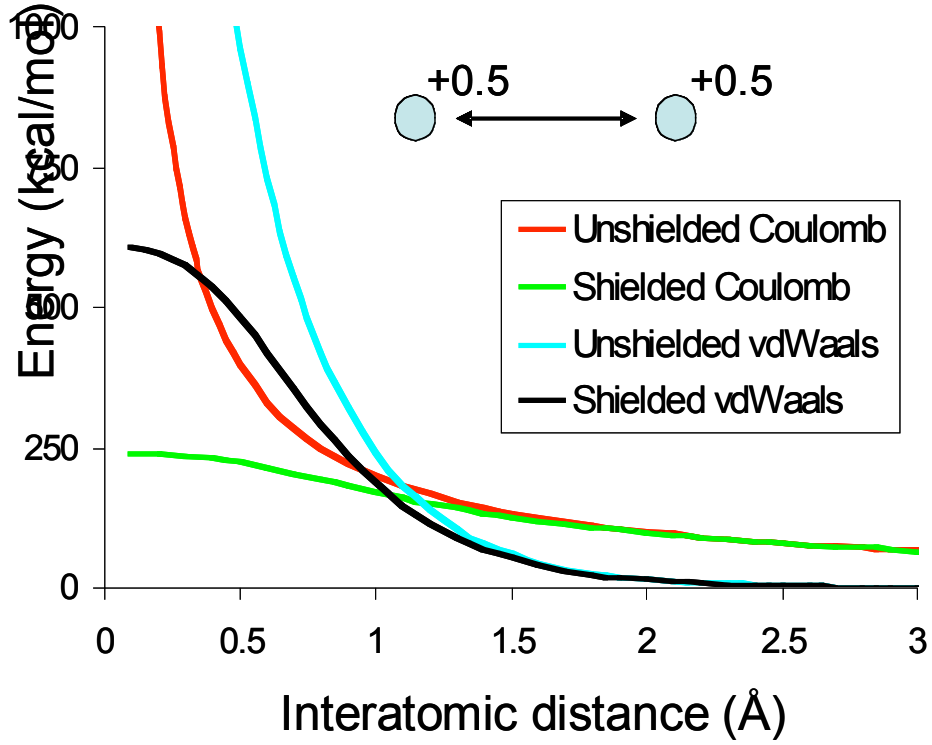
Nonbonded interactions



Non-reactive force field: ignore vdWaals and Coulomb interactions between atoms sharing a bond (I-j, j-k, k-l and l-m) or a valence angle (I-k, j-l and k-m).
These exception rules are very awkward when trying to describe reactions.

ReaxFF: calculate nonbonded interactions between *all* atom pairs, regardless of connectivity.
To avoid excessive repulsive/attractive nonbonded interactions at short distances both Coulomb and van der Waals interactions are shielded in ReaxFF.

Shielded vdWaals and Coulomb interactions



$$E_{Coulomb} = C \cdot \frac{q_i \cdot q_j}{\left\{ r_{ij}^3 + \left(1/\gamma_{ij}\right)^3 \right\}^{1/3}}$$

Shielded Coulomb potential

vdWaals: Shielded Morse potential

- For metals ReaxFF only uses bond energy, overcoordination, vdWaals and Coulomb-terms (no angle or dihedrals)
- vdWaals and overcoordination terms serve as a density-dependent repulsive term (as used in EAM-potentials [Daw and Baskes, PRB 1984]), allowing ReaxFF to describe bulk metals
- We have recently added an additional, repulsive Morse at very short distances and removed the vdWaals shielding to avoid Coulomb-collapse at high energy and density

Charge polarization

- Assign one electronegativity and hardness to each element; optimize these parameters against QM-charge distributions
- Use system geometry in solving electronegativity equilibration equations in every iteration

$$\frac{\partial E}{\partial q_1} = \chi_1 + 2q_1\eta_1 + C\cdot\sum_{j=1}^{n}\frac{q_j}{\left(r_{1,j}^3 + \left(\frac{1}{\gamma_{1,j}}\right)^3\right)^{\frac{1}{3}}}$$

$$\frac{\partial E}{\partial q_2} = \chi_2 + 2q_2\eta_2 + C\cdot\sum_{j=1}^{n}\frac{q_j}{\left(r_{2,j}^3 + \left(\frac{1}{\gamma_{2,j}}\right)^3\right)^{\frac{1}{3}}}$$

.....

.....

$$\frac{\partial E}{\partial q_n} = \chi_n + 2q_n\eta_n + C\cdot\sum_{j=1}^{n}\frac{q_j}{\left(r_{n,j}^3 + \left(\frac{1}{\gamma_{n,j}}\right)^3\right)^{\frac{1}{3}}}$$

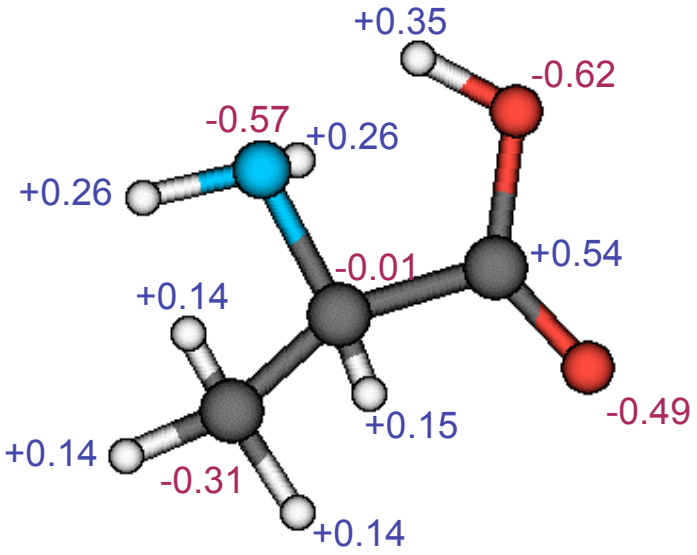
$$\sum_{i=1}^{n} q_i = 0$$

EEM-method (Mortier et al., JACS 1986); shielding: Janssens et al. J.Phys.Chem. 1995.

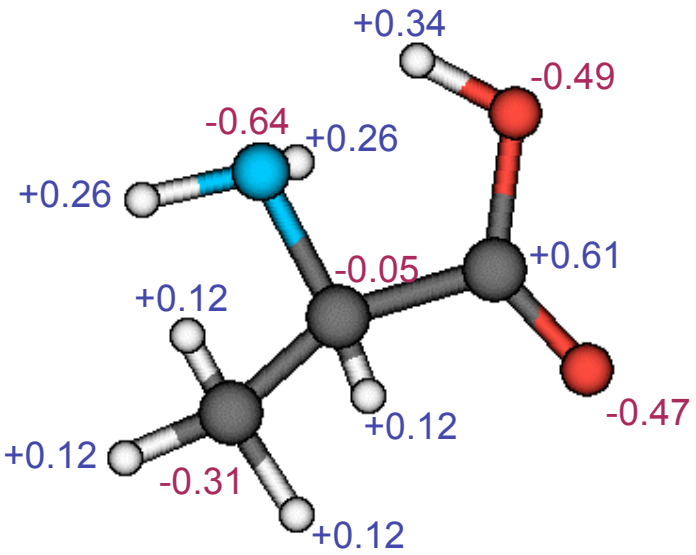
Similar to Qeq-method (Rappe and Goddard, J. Phys. Chem. 1991) with empirical shielding correction.

χ: atom electronegativity
η: atom hardness
γ: shielding parameter
r: interatomic distances
q:atom charge

ReaxFF charges



QM
Mulliken charges
DFT; 6-31G**

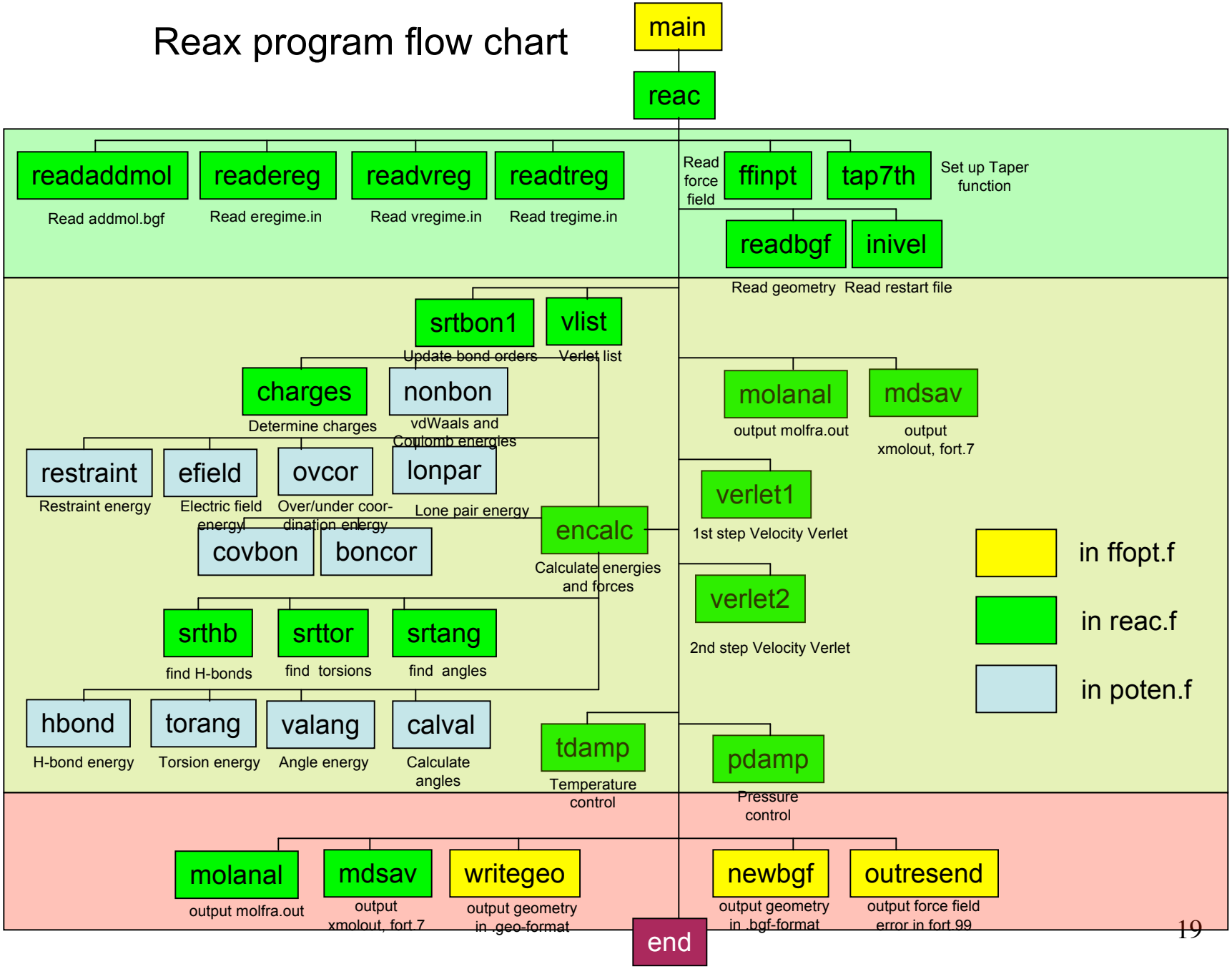


- Good reproduction of Mulliken charges (similar concepts)
- Combined with 1-2 Coulomb-interactions, this enables ReaxFF to simulate polarization effects on local chemistry
- EEM/Qeq methods work well around equilibrium; incorrect description of charge flow at high compression and dissociation (Chen and Martinez, Chem.Phys.Lett. 2006)
- Most expensive part of the reactive force field; needs to be updated every MD-step and forces sub-femtosecond steps

ReaxFF program structure

- Written in Fortran-77
- Library independent
- Text-based interface (graphical interface is developed within CMDF)
- Installed on various computers and operating systems (Linux, Windows, Macs)
- Code divided in 6 parts:
    - reac.f (10640 lines): general MD routines
    - poten.f (3034 lines): energy equations
    - ffopt.f (1581 lines): force field optimization
    - shanno (1718 lines): energy minimization
    - vibra.f (1194 lines): vibrational frequencies
    - blas.f (613 lines): BLAS-routines
    - program parameters in cbka.blk

Reax program flow chart



Overview ReaxFF in- and output files

General

Mandatory input files

- geo (input geometry)
- control (run control parameters)
- ffield (force field parameters)
- exe (UNIX-script)

geo-file for non-periodic system

BIOGRF version and structure identifier

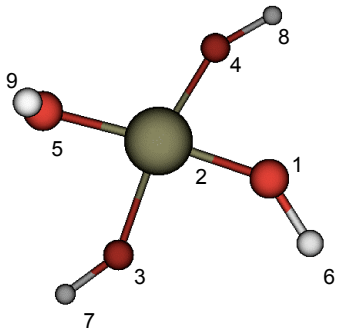
Atom types and cartesian coordinates

Ignored by Reax

Relevant to Reax

Closing line

```
BIOGRF 200
DESCRP ZrOH4
REMARK Created by jag2bgf from file: min.out
FORMAT ATOM   (a6,1x,i5,1x,a5,1x,a3,1x,a1,1x,a5,3f10.5,1x,a5,i3,i2,1x,f8.5)
HETATM    1 O            40.90831  38.41349  38.76651 O   1 1 -0.69047
HETATM    2 Zr           40.06262  39.84127  39.78197 Zr  1 1  1.45708
HETATM    3 O            41.51578  40.34790  40.99126 O   1 1 -0.69047
HETATM    4 O            38.59306  39.47050  41.01718 O   1 1 -0.69047
HETATM    5 O            39.46555  41.52856  39.00344 O   1 1 -0.69047
HETATM    6 H            41.76389  37.93562  38.81338 H   1 1  0.32620
HETATM    7 H            42.01707  41.16090  41.20659 H   1 1  0.32620
HETATM    8 H            38.50293  39.39880  41.99107 H   1 1  0.32620
HETATM    9 H            38.67137  42.09864  39.06290 H   1 1  0.32620
FORMAT CONECT (a6,12i6)
CONECT    1    2    6
CONECT    2    1    3    4    5
CONECT    3    2    7
CONECT    4    2    8
CONECT    5    2    9
CONECT    6    1
CONECT    7    3
CONECT    8    4
CONECT    9    5
UNIT ENERGY   kcal
ENERGY       -940.319333
END
```



$Zr(OH)_4$-cluster

Ignored by Reax

Connection table and system energy (ignored by Reax)

- for non-periodic system (i.e. big periodic box)
- lines can be organised in any order
- Reax units: Å and kcal/mol

geo-file for periodic system

XTLGRF version and structure identifier

Cell coordinates

Atom types and cartesian coordinates

Ignored by Reax

Relevant to Reax

Closing line

```
XTLGRF 200
DESCRP BaZrO3_0
REMARK BGF file created by Cerius2
FORMAT ATOM   (a6,1x,i5,1x,a5,1x,a3,1x,a1,1x,a5,3f10.5,1x,a5,i3,i2,1x,f8.5)
CRYSTX    4.24453   4.24453   4.24453  90.00000  90.00000  90.00000
HETATM    1 Ba          0.00000   0.00000   0.00000  Ba  1 1  0.00000
HETATM    2 Zr          2.12226   2.12226   2.12226  Zr  1 1  0.00000
HETATM    3 O           2.12226   2.12226   0.00000  O   1 1  0.00000
HETATM    4 O           2.12226   0.00000   2.12226  O   1 1  0.00000
HETATM    5 O           0.00000   2.12226   2.12226  O   1 1  0.00000
FORMAT CONECT (a6,12i6)
CONECT    1    2    2    2    2    2    2    2    2    3    3    3
CONECT    3    4    4    4    4    5    5    5    5    0    1    0
CONECT    1    0    1    0    1    0    1    0    1
CONECT    2    1    1    1    1    1    1    1    1    3    3    4
CONECT    4    5    5
CONECT    3    1    1    1    1    2    2
CONECT    4    1    1    1    1    2    2
CONECT    5    1    1    1    1    2    2
UNIT ENERGY   kcal
ENERGY       -785.823281
END
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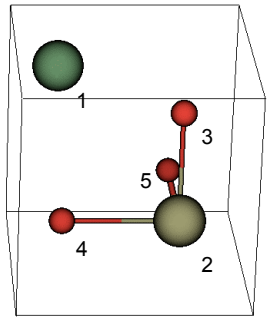


$BaZrO_3$-crystal

Connection table and system energy (ignored by Reax) Reax can handle unit cells.

control-file

```
# General parameters
      1 imetho    0: Normal MD-run 1: Energy minimisation 2:MD-energy minimisation
      1 igeofo    0:xyz-input geometry 1: Biograf input geometry 2: xmol-input geometry
 80.000 axis1     a (for non-periodical systems)
 80.000 axis2     b (for non-periodical systems)
 80.000 axis3     c (for non-periodical systems)
 0.0050 cutof2    BO-cutoff for valency angles and torsion angles
  0.300 cutof3    BO-cutoff for bond order for graphs
      3 icharg    Charges. 1:EEM 2:- 3: Shielded EEM 4: Full system EEM
     25 irecon    Frequency of reading control-file
      0 ixmolo    0: only x,y,z-coordinates in xmolout  1: molnr. in xmolout
# MD-parameters
      1 imdmet    MD-method. 1:Velocity Verlet+Berendsen 2:Hoover-Nose;3:NVE 4: NPT
  0.250 tstep     MD-time step (fs)
0100.00 mdtemp    1st MD-temperature
      2 itdmet    0: T-damp atoms 1: Energy cons 2:System 3: Mols 4: Anderson
    1.0 tdamp1    1st Berendsen/Anderson temperature damping constant (fs)
0000.00 mdpres    MD-pressure (MPa)
00100.0 pdamp1    Berendsen pressure damping constant (fs)
0001000 nmdit     Number of MD-iterations
  00001 ichupd    Charge update frequency
    001 iout1     Output to unit 71 and unit 73
   0050 iout2     Save coordinates
      1 iravel    1: Random initial velocities
 001000 iout6     Save velocity file
 000025 irten     Frequency of removal of rotational and translational energ
# MM-parameters
2.00000 endmm     End point criterium for MM energy minimisation
-000001 imaxmo    > 0: Maximum movement 0: Conjugate gradient < 0: MD-minimization
  00100 imaxit    Maximum number of iterations
1.00050 celopt    Cell parameter change
      0 icelo2    Change all cell parameters (0) or only x/y/z axis (1/2/3)
# FF-opt parameters
 0.0100 parext    Parameter optimization: extrapolation
      0 icelop    0: No cell parameter optimisation 1:Cell parameter optimisation
      1 igeopt    0: Always use same start gemetries 1:Use latest geometries
```

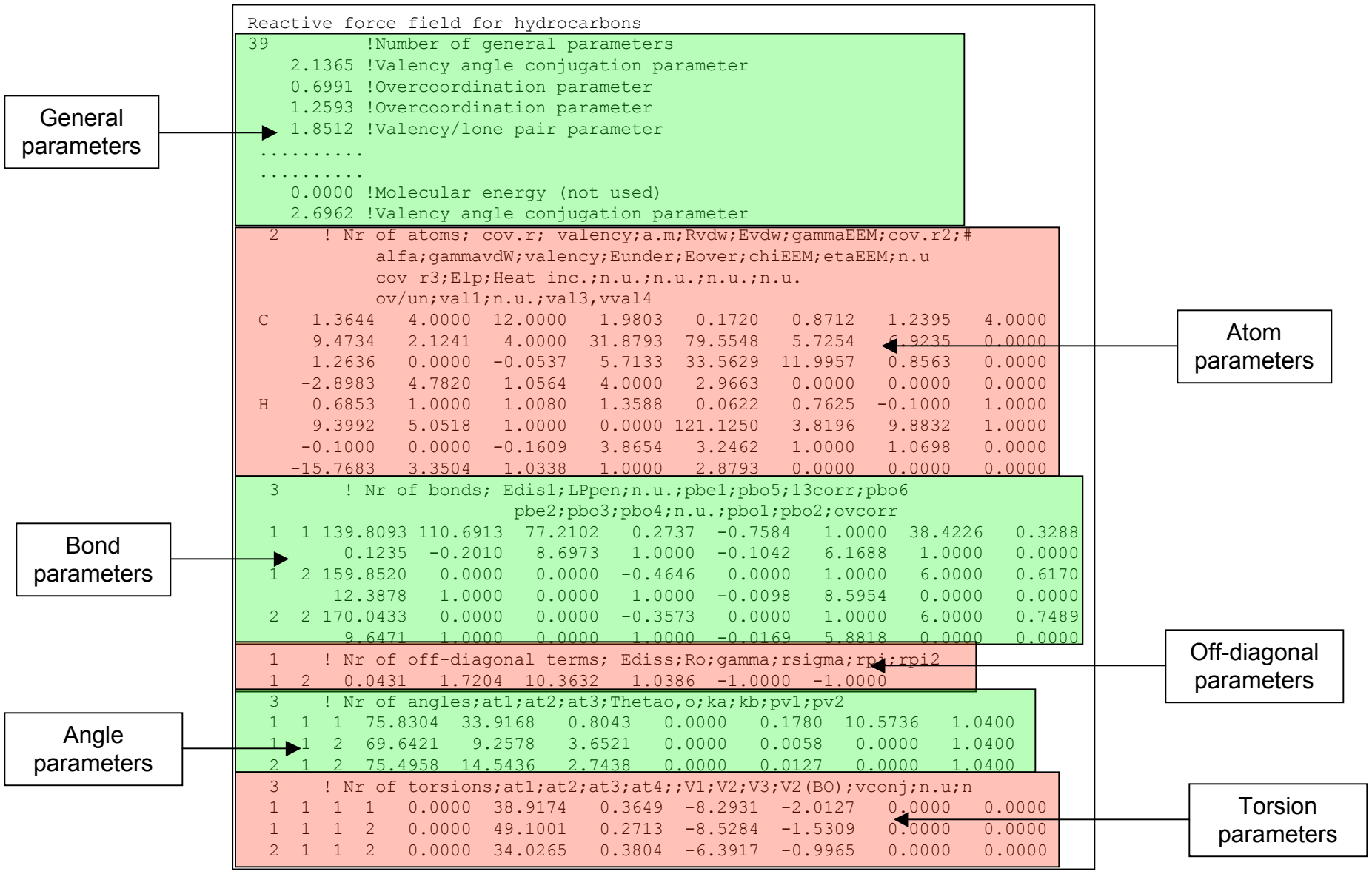
Parameter description (ignored by Reax)

Parameter value

Parameter name

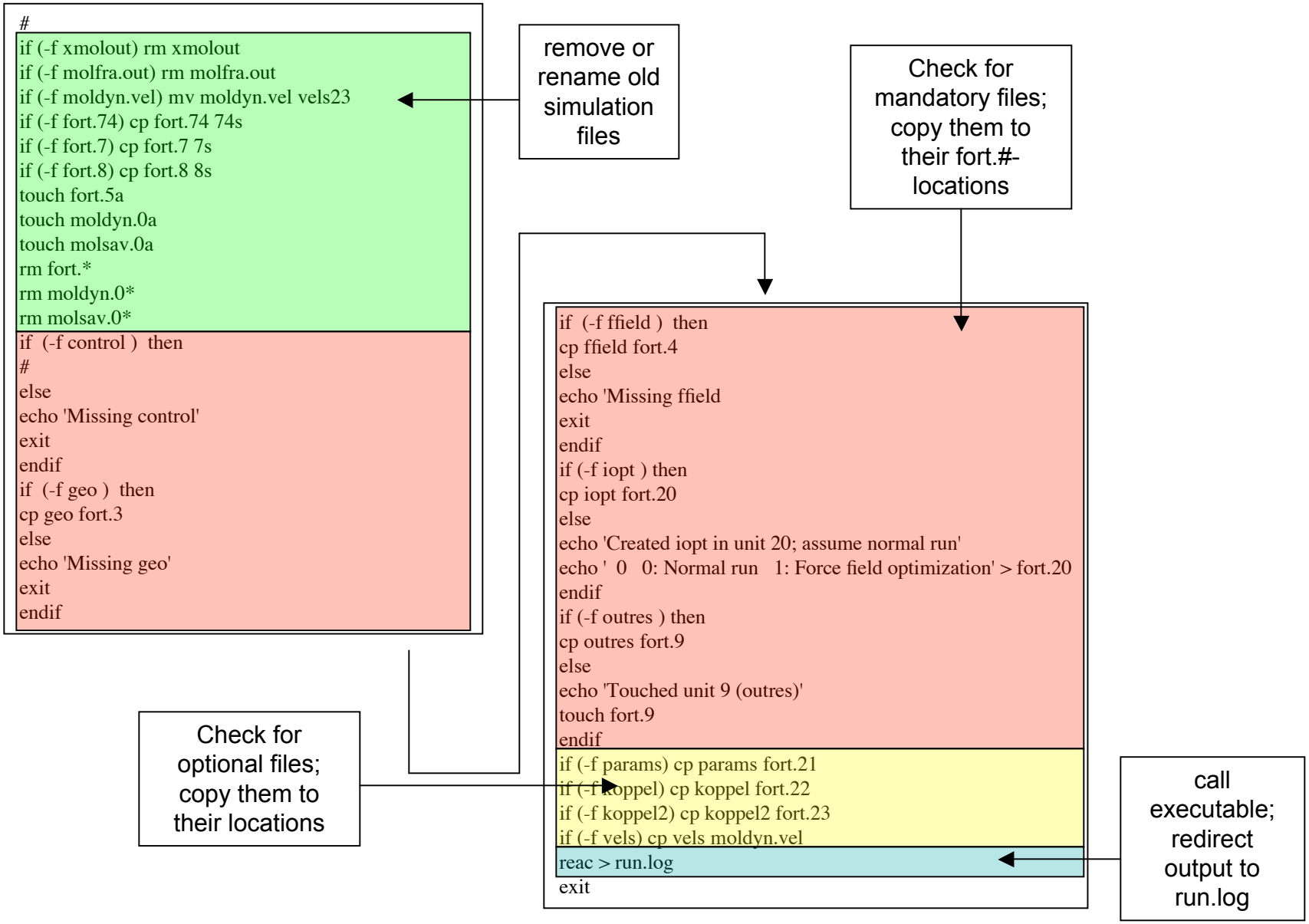
- lines can be organised in any order
- left-out keywords are given default value (see Manual)
- **Beware: control-file is read during simulations**

ffield-file



- Format sensitive text-file
- Hydrocarbon force field: about 70 independent parameters

exe-file



- Similar scripts available for Windows

General output files

- Connection table (fort.7, fort.8)
- Trajectory (xmolout)
- Molecular composition (molfra.out)
- run.log (generated by exe-script)
- output geometry in .bgf (fort.90, $DESCRP.bgf), .geo (fort.98, $DESCRP.geo), MOPAC (output.MOP) and .pdb (output.pdb) formats

Connection tables (fort.7, fort.8)

Atom number

Connection table

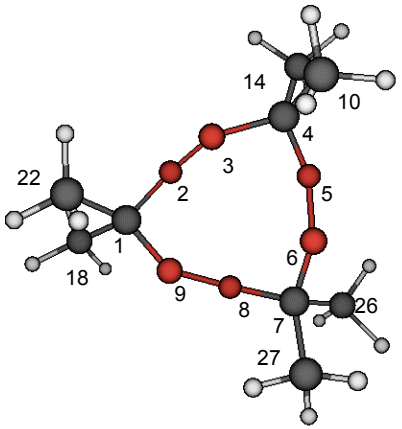
Bond orders

Number of lone pairs

33 TATP Iteration: 1 #Bonds: 5

1	1	2	9	18	22	0	1	1.053	1.098	0.974	0.963	0.000	4.089	0.000	0.451
2	3	1	3	0	0	0	1	1.053	0.751	0.000	0.000	0.000	1.845	2.000	-0.264
3	3	2	4	0	0	0	1	0.751	0.935	0.000	0.000	0.000	1.721	2.000	-0.274
4	1	3	5	10	14	0	1	0.935	1.133	0.959	1.002	0.000	4.031	0.000	0.448
5	3	4	6	0	0	0	1	1.133	0.578	0.000	0.000	0.000	1.752	2.000	-0.298
6	3	5	7	0	0	0	1	0.578	1.071	0.000	0.000	0.000	1.681	2.000	-0.297
7	1	6	8	26	27	0	1	1.071	1.046	1.001	0.983	0.000	4.102	0.000	0.453
8	3	7	9	0	0	0	1	1.046	0.646	0.000	0.000	0.000	1.722	2.000	-0.266
9	3	1	8	0	0	0	1	1.098	0.646	0.000	0.000	0.000	1.786	2.000	-0.302
10	1	4	11	12	13	0	1	0.959	0.971	0.981	0.978	0.000	3.898	0.000	-0.299
11	2	10	0	0	0	0	1	0.971	0.000	0.000	0.000	0.000	0.973	0.000	0.135
12	2	10	0	0	0	0	1	0.981	0.000	0.000	0.000	0.000	0.982	0.000	0.091
13	2	10	0	0	0	0	1	0.978	0.000	0.000	0.000	0.000	0.979	0.000	0.123
14	1	4	15	16	17	0	1	1.002	0.977	0.973	0.987	0.000	3.941	0.000	-0.314
15	2	14	0	0	0	0	1	0.977	0.000	0.000	0.000	0.000	0.978	0.000	0.117
16	2	14	0	0	0	0	1	0.973	0.000	0.000	0.000	0.000	0.974	0.000	0.159
17	2	14	0	0	0	0	1	0.987	0.000	0.000	0.000	0.000	0.988	0.000	0.099
18	1	1	19	20	21	0	1	0.974	0.982	0.981	0.973	0.000	3.914	0.000	-0.316
19	2	18	0	0	0	0	1	0.982	0.000	0.000	0.000	0.000	0.983	0.000	0.094
20	2	18	0	0	0	0	1	0.981	0.000	0.000	0.000	0.000	0.981	0.000	0.155
21	2	18	0	0	0	0	1	0.973	0.000	0.000	0.000	0.000	0.974	0.000	0.114
22	1	1	23	24	25	0	1	0.963	0.980	0.981	0.983	0.000	3.912	0.000	-0.312
23	2	22	0	0	0	0	1	0.980	0.000	0.000	0.000	0.000	0.983	0.000	0.149
24	2	22	0	0	0	0	1	0.981	0.000	0.000	0.000	0.000	0.985	0.000	0.087
25	2	22	0	0	0	0	1	0.983	0.000	0.000	0.000	0.000	0.984	0.000	0.143
26	1	7	28	29	30	0	1	1.001	0.975	0.967	0.985	0.000	3.932	0.000	-0.319
27	1	7	31	32	33	0	1	0.983	0.986	0.976	0.987	0.000	3.938	0.000	-0.295
28	2	26	0	0	0	0	1	0.975	0.000	0.000	0.000	0.000	0.977	0.000	0.154
29	2	26	0	0	0	0	1	0.967	0.000	0.000	0.000	0.000	0.967	0.000	0.111
30	2	26	0	0	0	0	1	0.985	0.000	0.000	0.000	0.000	0.987	0.000	0.096
31	2	27	0	0	0	0	1	0.986	0.000	0.000	0.000	0.000	0.989	0.000	0.127
32	2	27	0	0	0	0	1	0.976	0.000	0.000	0.000	0.000	0.978	0.000	0.087
33	2	27	0	0	0	0	1	0.987	0.000	0.000	0.000	0.000	0.989	0.000	0.152

63.9132746 12. 87.9132747 1.98401163E-06



Atom type

Molecule number

Total bond order

Charge

Trajectory (xmolout)

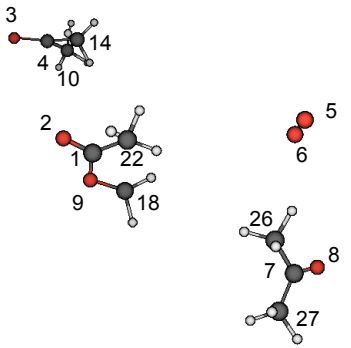
Nr. of atoms

Iteration

```
 33
 TATP                                  50000  -3263.2723  15.00  15.00  15.00  90.00  90.00  90.00
 C     8.03336   10.80257    4.49936    1
 O     7.06006   11.24892    5.00919    1
 O     4.56231    4.18113    9.18128    2
 C     5.82196    3.79677    9.09669    2
 O    -0.05164   -0.97661    5.55002    3
 O    -0.25853   -2.07159    5.08345    3
 C    14.91122   10.77409    0.43456    4
 O    15.79143    9.95465    0.55806    4
 O     7.88891    9.67888    3.58924    1
 C     7.08457    4.54261    9.04068    2
 H     6.82569    5.68357    9.14567    2
 H     7.76850    4.70124    9.69060    2
 H     7.54678    4.21871    8.15129    2
 C     6.52194    2.55547    8.86178    2
 H     6.06203    1.74448    8.28566    2
 H     7.35850    2.74576    8.36628    2
 H     6.61070    2.15807   10.04076    2
 C     9.10863    8.84173    3.18941    1
 H    10.04311    9.11621    3.67890    1
 H     8.96150    7.74381    3.06231    1
 H     9.36469    8.98250    2.09728    1
 C     9.25406   11.66721    4.94408    1
 H     9.64599   11.38664    5.92819    1
 H    10.23713   11.48547    4.57649    1
 H     8.73306   12.71015    5.21007    1
 C    14.32414   11.52220   -0.81138    4
 C    14.21203   11.50768    1.58922    4
 H    -0.97411   12.63100   -0.71155    4
 H    -0.04442   11.47791   -1.74049    4
 H    -1.58723   10.95248   -1.15750    4
 H    -1.79775   11.08963    1.84645    4
 H    -0.22268   11.43923    2.56322    4
 H    -0.87217   12.[illegible]0255    1.43429
```

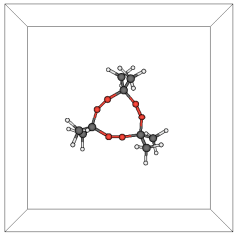
System energy

Cell parameters



O_2, 2 acetone and 1 $C_3H_5O_2$

xmol2ppm-script



Atom types

Cartesian coordinates

Molecule number

- viewable in molden, vmd, Xmol, etc.

Molecular composition (molfra.out)

from control-file (cutof3)

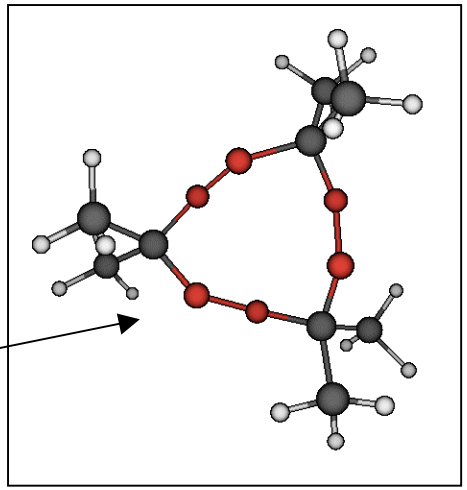
Bond order cutoff: 0.3000

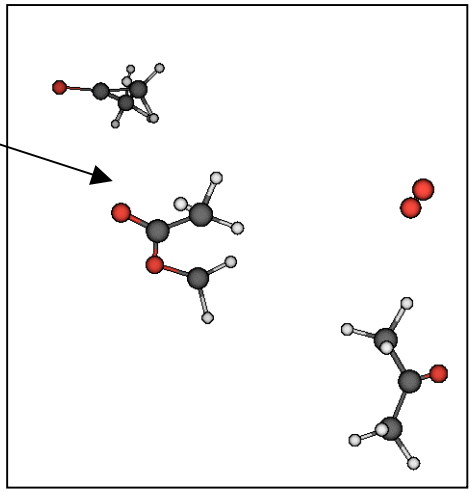
Iteration	Freq.	Molecular formula	Molecular mass
0	1 x	C9H18O6	222.1380

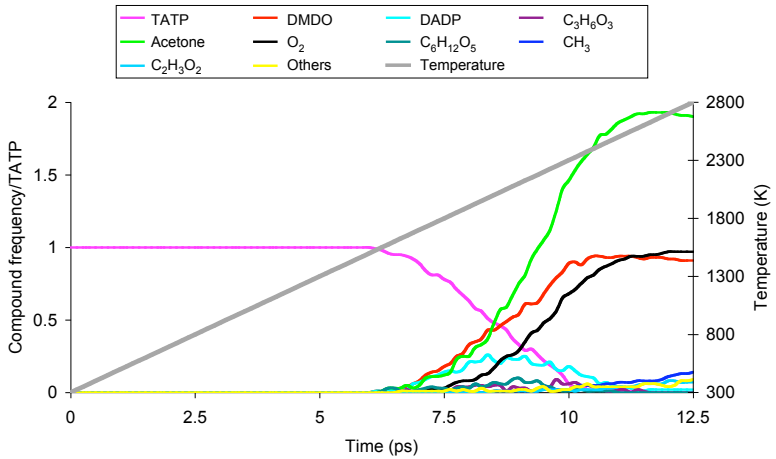
Total number of molecules: 1
Total number of atoms: 33
Total system mass: 222.138

Iteration	Freq.	Molecular formula	Molecular mass
50000	1 x	C3H6O2	74.0460
50000	2 x	C3H6O	58.0470
50000	1 x	O2	31.9980

Total number of molecules: 4
Total number of atoms: 33
Total system mass: 222.138







molfraanal-script

MD-simulations

fort.71-file: system energy, temperature, pressure

Iter.	Nmol	Epot	Ekin	Etot	T(K)	Eaver(block)	Eaver(total)	Taver	Tmax	Pres(MPa)	sdev(Epot)	sdev(Eaver)	Tset	Timestep	RMSG	time
100	1	1 -3289.58	30.87	-3258.70	313.86	-3285.68	-3285.68	273.61	314.42	0.00	1.98	0.46	300.00	0.25	1.27	25.00
200	1	1 -3292.27	33.53	-3258.74	340.84	-3289.35	-3287.51	311.66	363.83	0.00	2.40	0.72	300.00	0.25	0.80	50.00
300	1	1 -3291.21	32.31	-3258.91	328.43	-3292.49	-3289.17	341.99	381.07	0.00	1.92	1.30	300.00	0.25	0.78	75.00
400	1	1 -3290.25	31.34	-3258.91	318.59	-3290.59	-3289.53	321.80	356.10	0.00	1.60	1.59	300.00	0.25	0.58	100.00

fort.73-file: partial energies

Iter.	Ebond	Eatom	Elp	Emol	Eval	Ecoa	Ehbo	Etors	Econj	Evdw	Ecoul	Echarge	Efield
100	-4495.45	-60.25	0.00	0.00	120.61	0.00	0.00	20.07	-8.58	1236.56	-240.51	137.98	0.00
200	-4484.40	-57.58	0.00	0.00	119.76	0.00	0.00	17.21	-8.72	1223.85	-236.11	133.73	0.00
300	-4474.43	-57.39	0.00	0.00	125.02	0.00	0.00	18.30	-8.75	1208.42	-237.07	134.68	0.00
400	-4486.77	-59.36	0.00	0.00	122.69	0.00	0.00	20.88	-8.24	1221.92	-237.12	135.76	0.00

Energy minimization

fort.57-file: system energy, RMSG, step size

rx1_r105

Iter.	Epot	Max.move	Factor	RMSG	nfc
0	-7207.7284997876	0.000000	0.500000	13.424820	1000
1	-7214.2627018726	106.356930	1.000000	10.432679	1000
2	-7218.4317016993	76.301119	0.796025	8.851187	1000
3	-7220.9056742882	57.483475	0.508797	8.069797	1000
4	-7222.7568731781	49.947151	0.403063	7.474607	1000
5	-7224.1327904854	50.986049	0.381101	6.648365	1025
6	-7225.0426836959	51.535409	0.351192	5.885714	1025
7	-7225.6569128515	50.185090	0.302759	5.444924	1025
8	-7226.1661405040	48.261841	0.269352	5.037754	1025
9	-7226.5961136940	46.007296	0.237568	4.615682	1025
10	-7226.9431268709	43.080605	0.203818	4.349515	1050

fort.58-file: partial energies

rx1_r105

Iter.	Eatom	Elopa	Ebond	Emol	Eval	Ecoa	Ehb	Etor	Econj	Evdw	Ecoul
0	-195.698	0.000	-9362.480	0.000	54.886	2.028	0.000	28.731	-144.496	2458.875	-64.591
1	-187.893	0.000	-9369.146	0.000	52.603	2.020	0.000	29.311	-146.823	2455.084	-64.125
2	-179.478	0.000	-9375.695	0.000	50.822	2.029	0.000	30.093	-148.833	2451.905	-63.711
3	-172.861	0.000	-9380.963	0.000	49.670	2.049	0.000	30.724	-150.273	2449.916	-63.416
4	-167.166	0.000	-9385.731	0.000	48.798	2.077	0.000	31.246	-151.442	2448.541	-63.175
5	-162.194	0.000	-9390.050	0.000	48.108	2.108	0.000	31.706	-152.403	2447.594	-62.968
6	-158.208	0.000	-9393.595	0.000	47.609	2.140	0.000	32.088	-153.096	2446.958	-62.794
7	-155.215	0.000	-9396.354	0.000	47.262	2.170	0.000	32.379	-153.545	2446.534	-62.654
8	-152.816	0.000	-9398.641	0.000	46.995	2.197	0.000	32.580	-153.866	2446.230	-62.539
9	-150.914	0.000	-9400.489	0.000	46.786	2.220	0.000	32.701	-154.106	2446.014	-62.448
10	-149.449	0.000	-9401.927	0.000	46.622	2.239	0.000	32.778	-154.286	2445.862	-62.381

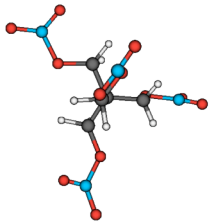
Examples

-Single molecules:
- minimization
- MD
- cookoff

-Periodic molecular systems:
- building
- compression
- piston simulations

-Combined molecular/condensed systems
-building
- MD

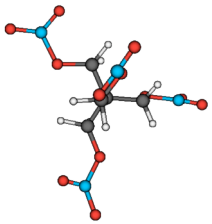
Single molecule simulations



PETN in 12.5x12.5x12.5 box
(PETN_minim)

t_{cpu}<<1 sec.

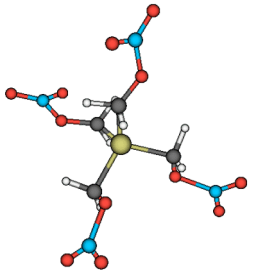
Minimization



Minimized PETN
(PETN_Si_minim)

Exchange
central C for Si

t_{cpu}<1 sec.



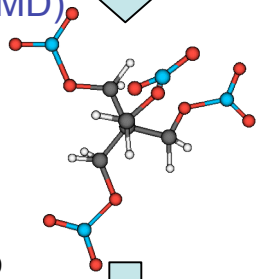
Si_{216}-cluster
(Si216_cluster_minim)

Directory name

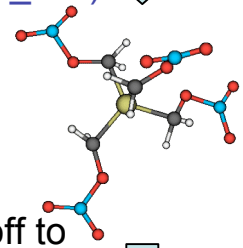
Simulation time on Mac 2.16 GHz
laptop with 2GB 667 MHz memory

2.5 ps. MD at 300K
(PETN_300K_MD)

t_{cpu}-=85 sec.

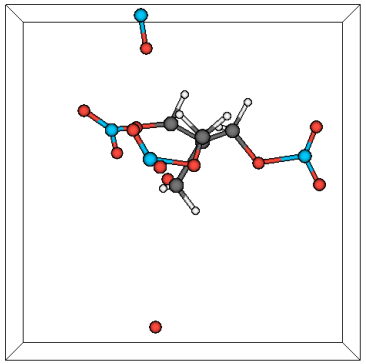


2.5 ps. MD at 300K
(PETN_Si_300K_MD)

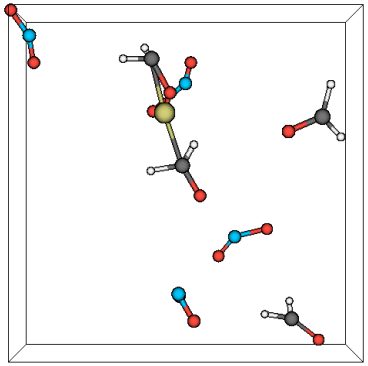


10 ps. MD-cookoff to
T=2000K
(PETN_cookoff)

t_{cpu}-=307 sec.

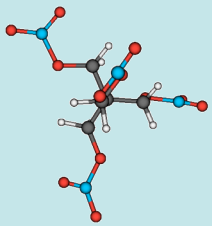


10 ps. MD-cookoff to
T=2000K
(PETN_Si_cookoff)



PETN_Si: highly energetic and sensitive Si-exchanged PETN analogon (Klapoetke et al. JACS 2007, **129**, 6908-6915

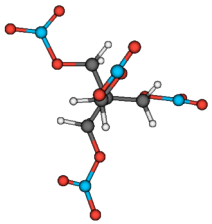
Single molecule simulations



Minimization

PETN in 12.5x12.5x12.5 box
(PETN_minim)

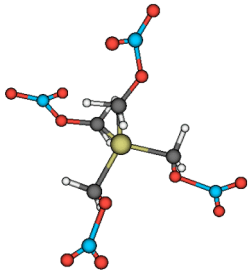
t_{cpu}<<1 sec.



Minimized PETN
(PETN_minim)

Exchange
central C for Si

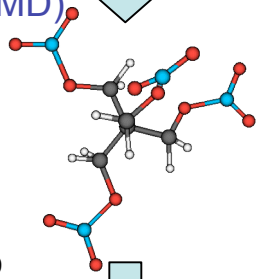
t_{cpu}<1 sec.



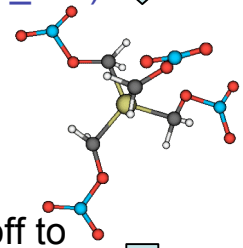
Minimized PETN_Si
(PETN_Si_minim)

2.5 ps. MD at 300K
(PETN_300K_MD)

t_{cpu}-=85 sec.

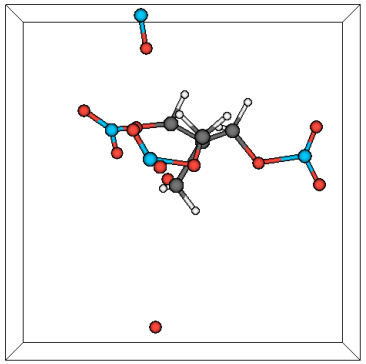


2.5 ps. MD at 300K
(PETN_Si_300K_MD)

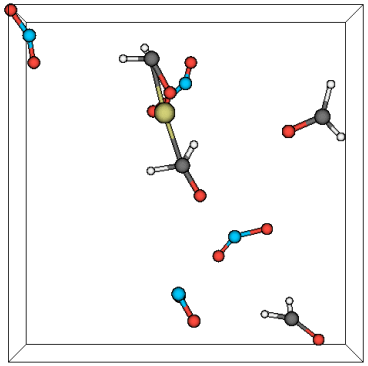


10 ps. MD-cookoff to
T=2000K
(PETN_cookoff)

t_{cpu}-=307 sec.



10 ps. MD-cookoff to
T=2000K
(PETN_Si_cookoff)



Input files

```
XTLGRF 200
DESCRP PETN
CRYSTX    12.50000   12.50000   12.50000   90.00   90.00
90.0
REMARK .bgf-file generated by xtob-script
FORMAT ATOM
(a6,1x,i5,1x,a5,1x,a3,1x,a1,1x,a5,3f10.5,1x,a5,i3,i2,1x,
HETATM     1 C     39.99909  39.99858  40.00188    C   1 1
0.0
HETATM     2 C     39.80751  40.09810  41.52432    C   1 1
0.0
HETATM     3 C     41.49125  40.11232  39.64758    C   1 1
0.0
....
....
HETATM    27 O     38.08038  36.41899  38.88316    O   1 1
0.0
HETATM    28 O     39.56796  44.75338  39.55450    O   1 1
0.0
HETATM    29 O     38.22313  43.4                  O   1 1
0.0
FORMAT CONECT (a6,12i6)
END
```

geo

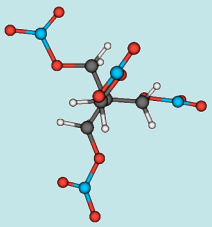
```
# General parameters
      1 itrans      0: do not back-translate atoms  1: back translate atoms
      1 icentr      0: keep position   1: put centre of mass in centre p
      1 imetho      0: Normal MD-run 1: Energy minimisation
      1 igeofo      0:xyz-input geometry 1: Biograf input geometry
      3 ixmolo      0: x,y,z-coordinates in xmolout  3:
x,y,z+mol.nr.+Estrain
# MM-parameters
0.50000 endmm       End point criterium for MM energy minimisation
  00000 imaxmo      <0 MD-based >0 Steepest descent 0: Conjugate gradient
  00100 imaxit      Maximum number of iterations
    005 iout4       Frequency of structure output during minimisation
      0 iout5       1:Remove fort.57 and fort.58 files
1.00250 celopt      Cell parameter change
```

Relevant keyword
Default keyword

control

Other input files :
- exe (standard)
- ffield (from trainingsets/Si_PETN_inner)

Overview force field files in trainingsets:
Al_no_inner: 2006 Al/nitramine potential; describes nitramines, Al/H//C/N/O and Si/C/O/H interactions
Si_PETN_inner: 2008 Si_PETN inner wall (under development)



Minimization

PETN in 12.5x12.5x12.5 box
(PETN_minim)

t_{cpu}<<1 sec.

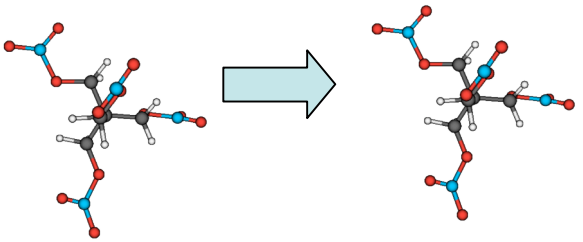
Output files

PETN

Iter.	Epot	Max.move	Factor	RMSG	nfc
0	-2857.8463056624	0.000000	0.500000	23.613638	0
1	-2865.1698944757	110.682535	10.230988	8.468166	0
2	-2866.6003869710	50.580457	0.085936	6.102469	0
3	-2867.0815824671	0.002128	1.274641	2.502796	0
4	-2867.9319327036	0.001444	9.748955	3.161622	0
5	-2868.1956017389	0.002013	1.408529	2.433199	0
6	-2868.3816691278	0.005765	0.546038	3.090506	0
7	-2868.5893256912	0.006178	0.729279	2.951746	0
8	-2869.0667885032	0.002212	5.091302	1.252738	0
9	-2869.1147851940	0.000692	2.811574	1.645893	0
10	-2869.2000661672	0.004646	0.860948	2.303249	0
11	-2869.4046389150	0.001567	4.514527	2.730929	0
12	-2869.5182974881	0.005804	1.253071	1.802393	0
13	-2869.5659859295	0.001778	1.602192	1.627669	0
14	-2869.6557759388	0.001626	2.384846	1.598407	0
15	-2869.7001878832	0.001220	2.649286	1.249005	0
16	-2869.7283744473	0.002075	1.688906	0.843172	0
17	-2869.7891661797	0.000908	3.000000	1.375592	0
18	-2869.8145582051	0.000407	1.600054	0.624558	0
19	-2869.8573679648	0.001192	3.766324	1.437771	0
20	-2869.8708271492	0.001319	1.065667	0.480315	0

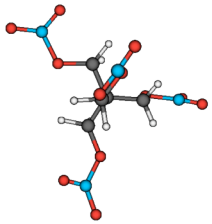
Minimization report

fort.57



Other output files:
- fort.7, fort.8: connection table
- fort.58: partial energies
- fort.73: final partial energies
- fort.90: final geometry (.bgf)
- xmolout: .xyz coordinates
- molfra.out : system composition

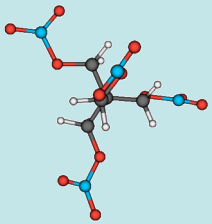
Single molecule simulations



PETN in 12.5x12.5x12.5 box
(PETN_minim)

Minimization

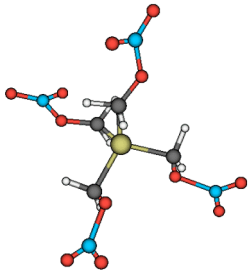
t_{cpu}<<1 sec.



Minimized PETN
(PETN_Si_minim)

Exchange
central C for Si

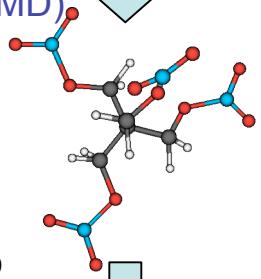
t_{cpu}<1 sec.



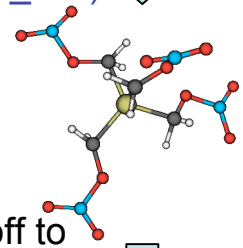
Minimized PETN_Si
(PETN_Si_minim)

2.5 ps. MD at 300K
(PETN_300K_MD)

t_{cpu}-=85 sec.

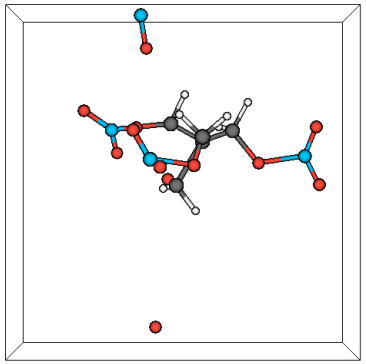


2.5 ps. MD at 300K
(PETN_Si_300K_MD)

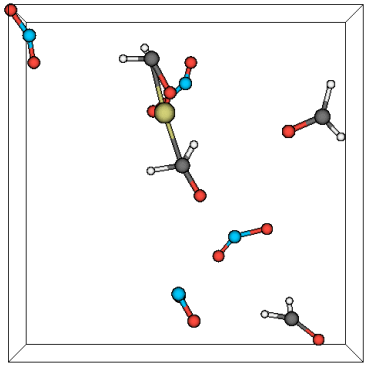


10 ps. MD-cookoff to
T=2000K
(PETN_cookoff)

t_{cpu}-=307 sec.



10 ps. MD-cookoff to
T=2000K
(PETN_Si_cookoff)



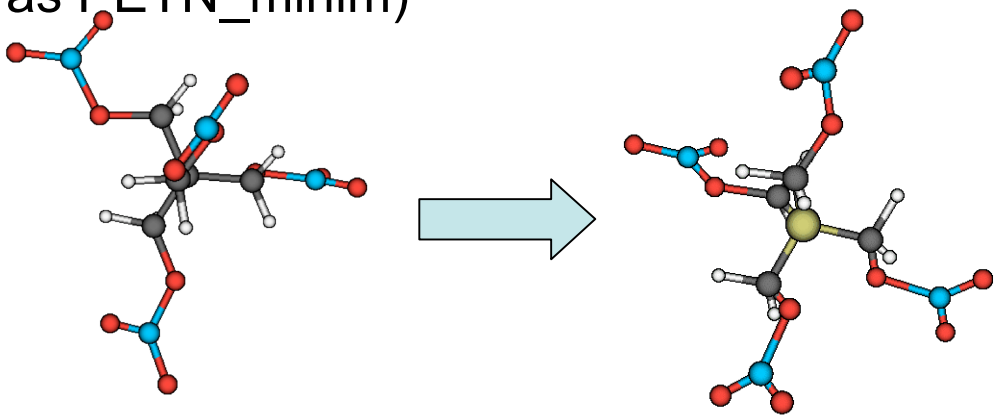
Input files

```
XTLGRF 200
DESCRP PETN_Si
REMARK .bgf-file generated by xtob-script
CRYSTX    12.50000   12.50000   12.50000   90.00000   90.00000   90.00000
FORMAT ATOM   (a6,1x,i5,1x,a5,1x,a3,1x,a1,1x,a5,3f10.5,1x,a5,i3,i2,1x,f8.5)
HETATM     1 Si                  6.24907   6.24824   6.25154    C   1 1  0.00000
HETATM     2 C                   6.07958   6.33339   7.77969    C   1 1  0.00000
HETATM     3 C                   7.73838   6.34985   5.87377    C   1 1  0.00000
HETATM     4 H                   6.26187   7.41337   8.08789    H   1 1  0.00000
HETATM     5 H                   8.31958   5.66348   6.57077    H   1 1  0.00000
……
END
```

geo (fort.90 from PETN_minim)

- Atom type 1 changed from C to Si

- Other input files : exe, ffield (standard)
  control (same as PETN_minim)



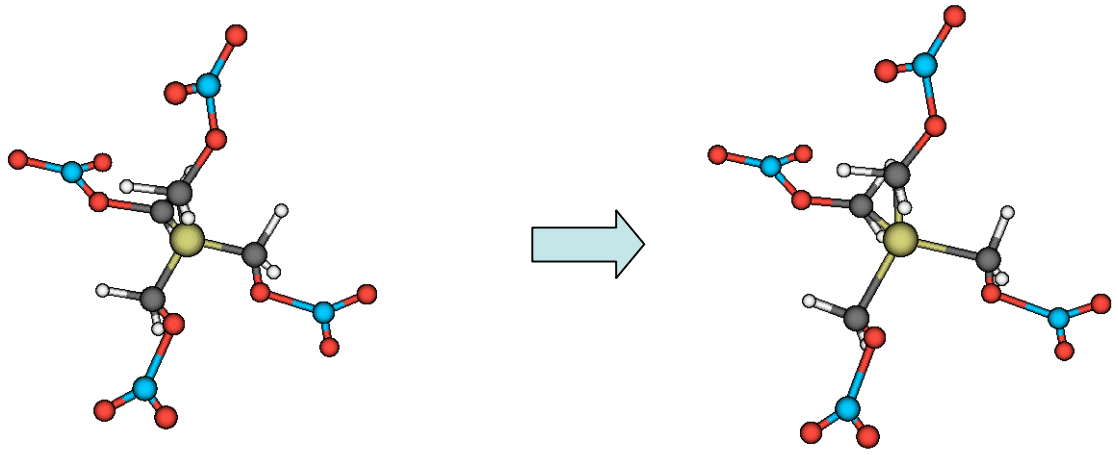
Output files

PETN_Si

Iter.	Epot	Max.move	Factor	RMSG	nfc
0	-2462.2931355145	0.000000	0.500000	38.353160	0
1	-2666.9306856910	305.393709	292.100576	61.788687	0
2	-2681.4094558847	572.929938	0.184190	27.008429	0
3	-2692.4766895412	0.038345	0.514299	17.912475	0
4	-2698.9665818152	0.015245	1.712551	25.222701	0
5	-2703.7222668757	0.020338	0.874622	16.647242	0
6	-2713.6184916061	0.010284	1.930882	19.846418	0
7	-2727.3838699098	0.019505	2.762917	15.087067	0
8	-2732.5221996455	0.012268	1.906405	17.022466	0
……					
92	-2812.4727698157	0.000681	1.779472	0.893753	0
93	-2812.5017799148	0.001306	3.035367	1.034961	0
94	-2812.5131763678	0.000677	1.760993	0.666916	0
95	-2812.5261664819	0.001902	1.041995	1.022934	0
96	-2812.5383363094	0.001257	1.976675	0.480811	0

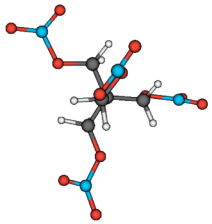
Minimization report

fort.57



Other output files:
- fort.7, fort.8: connection table
- fort.58: partial energies
- fort.73: final partial energies
- fort.90: final geometry (.bgf)
- xmolout: .xyz coordinates
- molfra.out : system composition

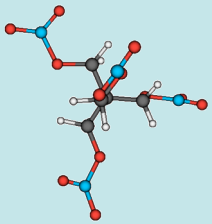
Single molecule simulations



PETN in 12.5x12.5x12.5 box
(PETN_minim)

Minimization

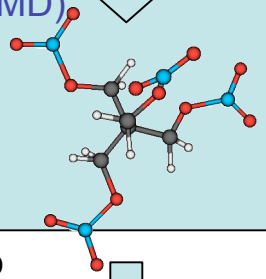
t_{cpu}<<1 sec.



Minimized PETN
(PETN_Si_minim)

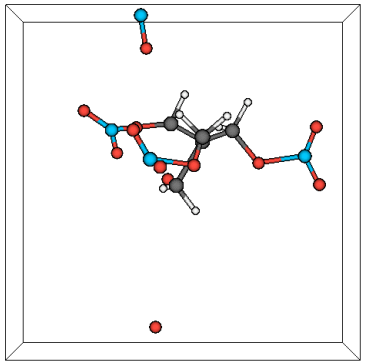
2.5 ps. MD at 300K
(PETN_300K_MD)

t_{cpu}-=85 sec.



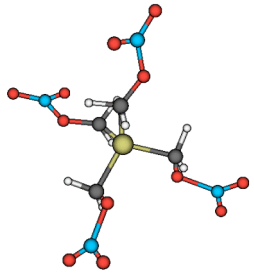
10 ps. MD-cookoff to
T=2000K
(PETN_cookoff)

t_{cpu}-=307 sec.



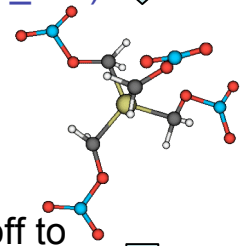
Exchange
central C for Si

t_{cpu}<1 sec.

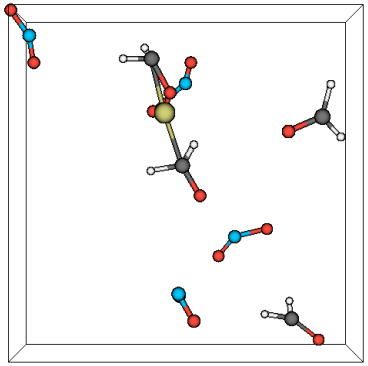


Minimized PETN_Si
(PETN_Si_minim)

2.5 ps. MD at 300K
(PETN_Si_300K_MD)



10 ps. MD-cookoff to
T=2000K
(PETN_Si_cookoff)



Input files

```
# General parameters
      1 itrans      0: do not back-translate atoms  1: back translate atoms
      0 imetho      0: Normal MD-run 1: Energy minimisation 2:MD-energy minimisation
      1 igeofo      0:xyz-input geometry 1: Biograf input geometry 2: xmol-input geometry
      3 ixmolo      0: only x,y,z-coordinates in xmolout  3: x,y,z+mol.nr.+Estrain
# MD-parameters
      1 imdmet      MD-method. 1:NVT/Berendsen thermostat 2:do not use;3:NVE 4: NPT/Berendsen
  0.250 tstep       MD-time step (fs)
0300.00 mdtemp      MD-temperature
      2 itdmet      0: T-damp atoms 1: Energy cons 2:System 3: Mols 4: Anderson 5: Mols+2
types
  100.0 tdamp1      1st Berendsen/Anderson temperature damping constant (fs)
……
0010000 nmdit       Number of MD-iterations
  00001 ichupd      Charge update frequency
    025 iout1       Output to unit 71 and unit 73
   0250 iout2       Save coordinates to xmolout
      0 ivels       1:Set vels and accels from moldyn.vel to zero
  00025 itrafr      Frequency of trarot-calls
      1 iout3       0: create moldyn.xxxx-files 1: do not create moldyn.xxxx-files
      1 iravel      1: Random initial velocities
 010000 iout6       Save velocity file
 000025 irten       Frequency of removal of rotational and translational energy
      0 npreit      Nr. of iterations in previous runs
  00.00 range       Range for back-translation of atoms
# MM-parameters

……
```

Relevant keyword
Default keyword

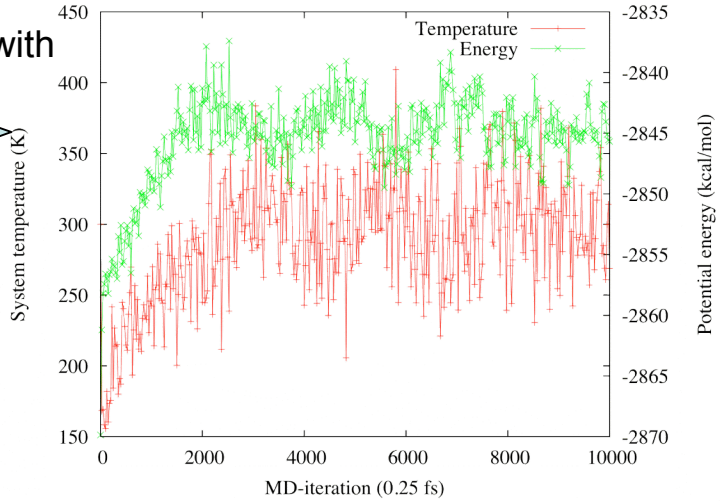
control

- Other input files : geo (fort.90 from PETN_minim), exe, ffield (standard)

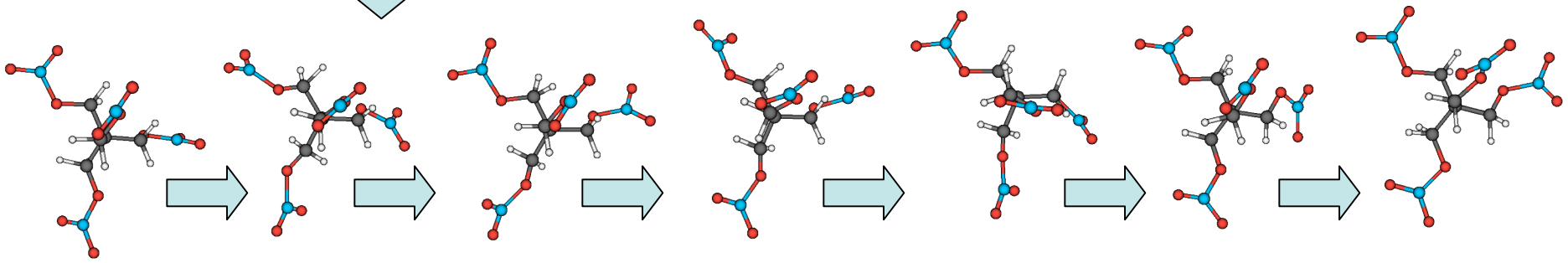
Output files

- fort.7, fort.8: connection table
- fort.71: energy, temperature data
- fort.73: final partial energies
- fort.90: final geometry (.bgf)
-molfra.out : system composition
- summary.txt: overview system properties
- xmolout: .xyz coordinates

Can be visualized with e.g. gnuplot

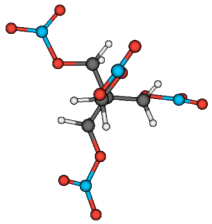


Can be visualized with e.g. molden, vmd



Iteration 0 Iteration 1750 Iteration 3500 Iteration 5250 Iteration 6000 Iteration 8500 Iteration 10000

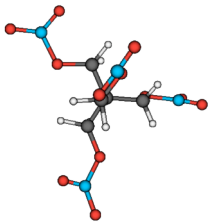
Single molecule simulations



PETN in 12.5x12.5x12.5 box
(PETN_minim)

Minimization

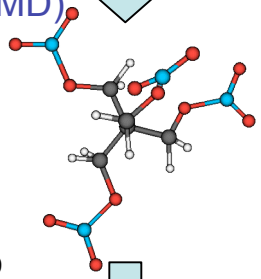
t_{cpu}<<1 sec.



Minimized PETN
(PETN_Si_minim)

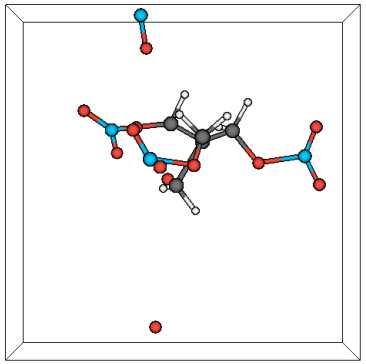
2.5 ps. MD at 300K
(PETN_300K_MD)

t_{cpu}-=85 sec.



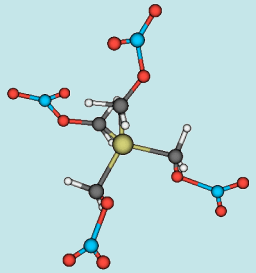
10 ps. MD-cookoff to
T=2000K
(PETN_cookoff)

t_{cpu}-=307 sec.



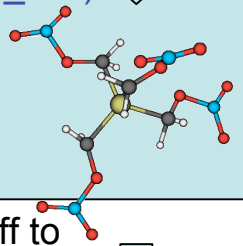
Exchange
central C for Si

t_{cpu}<1 sec.

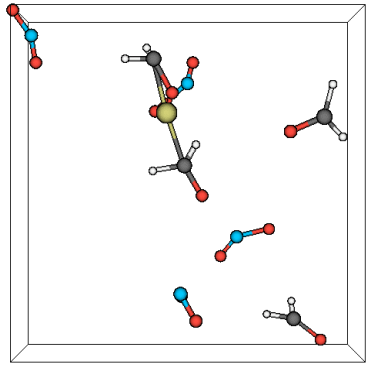


Minimized PETN_Si
(PETN_Si_minim)

2.5 ps. MD at 300K
(PETN_Si_300K_MD)



10 ps. MD-cookoff to
T=2000K
(PETN_Si_cookoff)



Input files

```
# General parameters
      1 itrans      0: do not back-translate atoms  1: back translate atoms
      0 imetho      0: Normal MD-run 1: Energy minimisation 2:MD-energy minimisation
      1 igeofo      0:xyz-input geometry 1: Biograf input geometry 2: xmol-input geometry
      3 ixmolo      0: only x,y,z-coordinates in xmolout  3: x,y,z+mol.nr.+Estrain
# MD-parameters
      1 imdmet      MD-method. 1:NVT/Berendsen thermostat 2:do not use;3:NVE 4: NPT/Berendsen
  0.250 tstep       MD-time step (fs)
0300.00 mdtemp      MD-temperature
      2 itdmet      0: T-damp atoms 1: Energy cons 2:System 3: Mols 4: Anderson 5: Mols+2
types
  100.0 tdamp1      1st Berendsen/Anderson temperature damping constant (fs)
……
0010000 nmdit       Number of MD-iterations
  00001 ichupd      Charge update frequency
    025 iout1       Output to unit 71 and unit 73
   0250 iout2       Save coordinates to xmolout
      0 ivels       1:Set vels and accels from moldyn.vel to zero
  00025 itrafr      Frequency of trarot-calls
      1 iout3       0: create moldyn.xxxx-files 1: do not create moldyn.xxxx-files
      1 iravel      1: Random initial velocities
 010000 iout6       Save velocity file
 000025 irten       Frequency of removal of rotational and translational energy
      0 npreit      Nr. of iterations in previous runs
  00.00 range       Range for back-translation of atoms
# MM-parameters

……
```

Relevant keyword
Default keyword

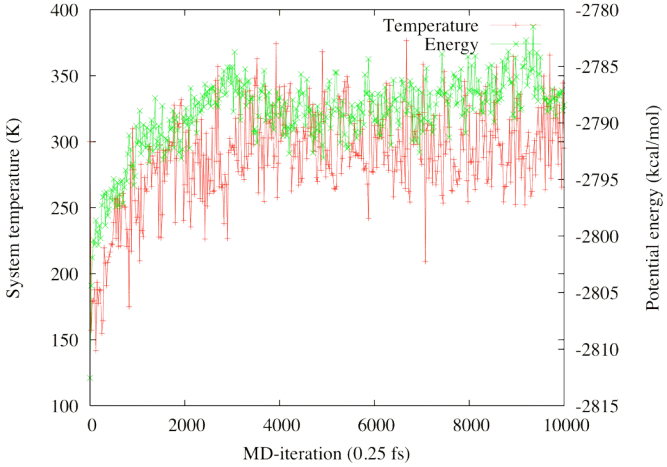
control

- Other input files : geo (fort.90 from PETN_Si_minim), exe, ffield (standard)

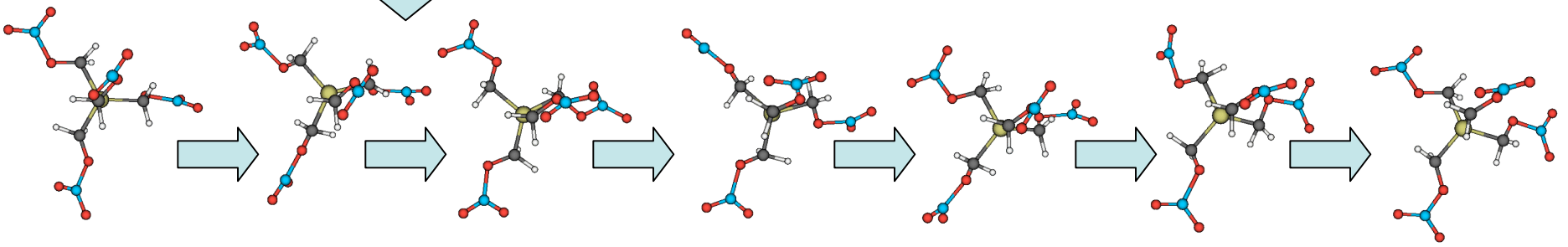
Output files

- fort.7, fort.8: connection table
- fort.71: energy, temperature data
- fort.73: final partial energies
- fort.90: final geometry (.bgf)
- molfra.out : system composition
- moldyn.vel, molsav.####: restart-files
- summary.txt: overview system properties
- xmolout: .xyz coordinates

Can be visualized with e.g. gnuplot

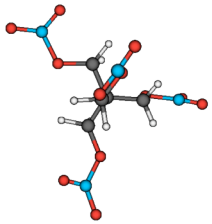


Can be visualized with e.g. molden, vmd



Iteration 0 Iteration 1750 Iteration 3500 Iteration 5250 Iteration 7000 Iteration 8500 Iteration 10000

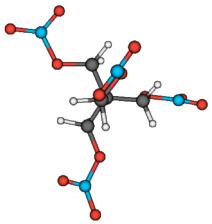
Single molecule simulations



PETN in 12.5x12.5x12.5 box
(PETN_minim)

Minimization

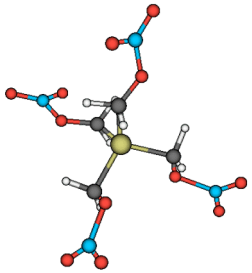
t_{cpu}<<1 sec.



Minimized PETN
(PETN_Si_minim)

Exchange
central C for Si

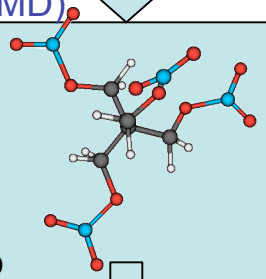
t_{cpu}<1 sec.



Minimized PETN_Si
(PETN_Si_minim)

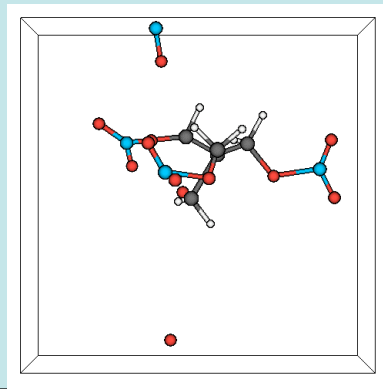
2.5 ps. MD at 300K
(PETN_300K_MD)

t_{cpu}-=85 sec.

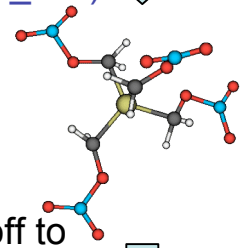


10 ps. MD-cookoff to
T=2000K
(PETN_cookoff)

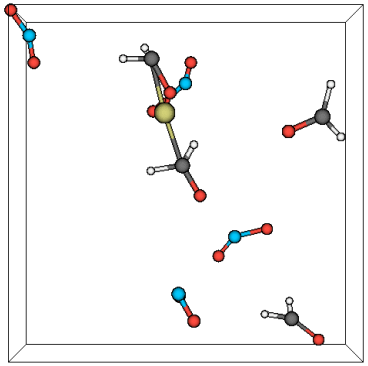
t_{cpu}-=307 sec.



2.5 ps. MD at 300K
(PETN_Si_300K_MD)

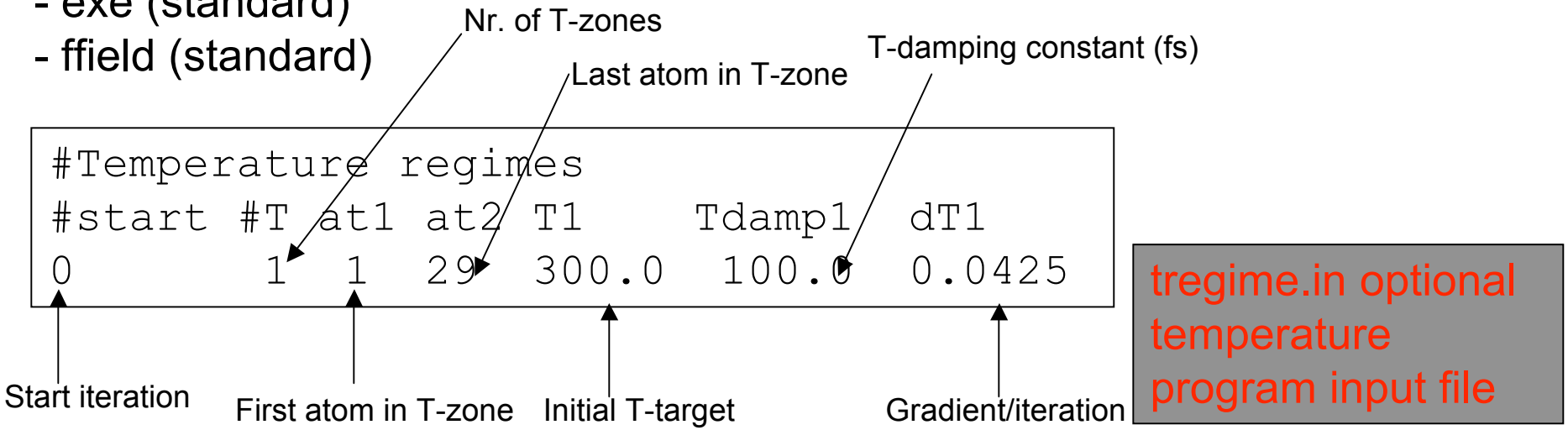


10 ps. MD-cookoff to
T=2000K
(PETN_Si_cookoff)



Input files

- tregime.in-file;
- control-file (mdstep=40000, other keywords from PETN_300K_MD)
- vels-restart file (copied from moldyn.vel from PETN_300K_MD)
- geo (copied from fort.90 from PETN_300K_MD)
- exe (standard)
- ffield (standard)



T_{target}(iteration 0) = 300K
T_{target}(iteration 40000) =2000K

Hierarchy: tregime.in-file overrides control-file

Input files (continued)

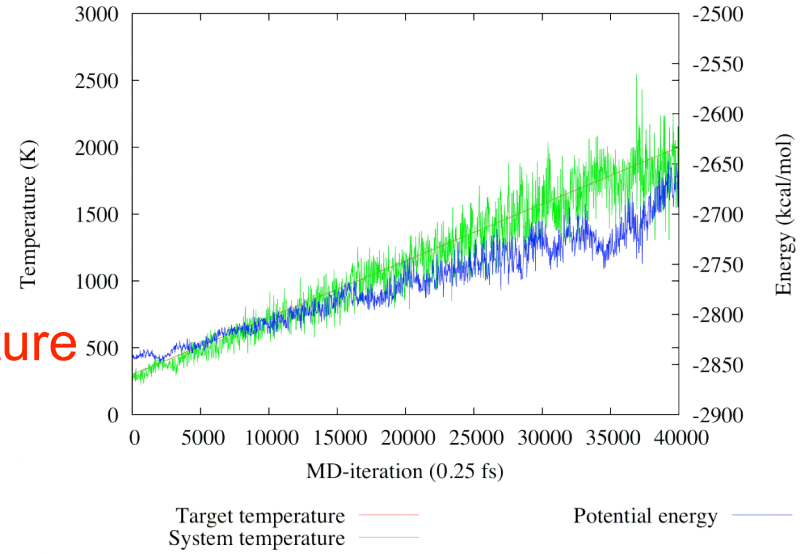
```
 Lattice parameters:
    12.50000000    12.50000000    12.50000000
    90.00000000    90.00000000    90.00000000
  29 Atom coordinates (Angstrom):
   0.615034599999870E+01   0.659324034446023E+01   0.595007781398092E+01 C
   0.612350096557127E+01   0.641983339984488E+01   0.751632941088376E+01 C
   0.759742589175836E+01   0.696800009368264E+01   0.542286334421500E+01 C
 ........
  Atom velocities (Angstrom/s):
   -0.555828196028097E+13   0.695401305107819E+13  -0.318609333550996E+13
   -0.321240017571219E+13  -0.808393568242614E+13   0.682465227335288E+12
   -0.235622402461510E+13   0.517918158076648E+13  -0.266985471476337E+12
 ........
  Atom accelerations (Angstrom/s**2):
   -0.860829435640501E+27   0.107864527094631E+28   0.110716570831586E+27
    0.324220055530896E+27   0.205818454355825E+28   0.901854732802793E+27
    0.205346886550601E+27   0.221825415740372E+28   0.236391224644222E+27
 ........
  Previous atom accelerations:
    0.000000000000000E+00   0.000000000000000E+00   0.000000000000000E+00
    0.000000000000000E+00   0.000000000000000E+00   0.000000000000000E+00
    0.000000000000000E+00   0.000000000000000E+00   0.000000000000000E+00
 ........
  MD-temperature (K):
    0.268748592153720E+03
  Connections, bond orders and lone pairs:
```

vels optional restart file

Hierarchy: vels overrides geo (beware !); geo overrides control-file

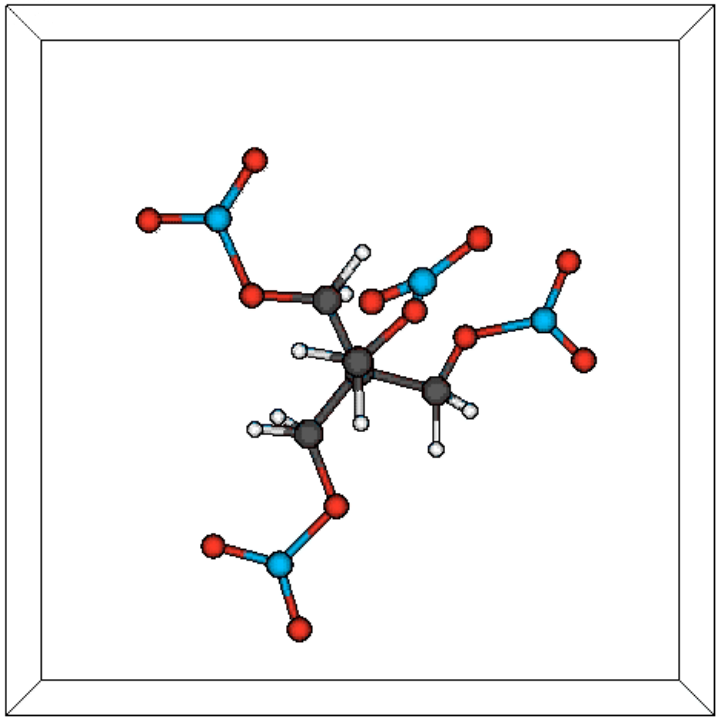
Output files

- fort.7, fort.8: connection table
- fort.71: energy, temperature data
- fort.73: final partial energies
- fort.75: overview target and system temperature
- fort.90: final geometry (.bgf)
- molfra.out : system composition
- moldyn.vel, molsav.####: restart-files
- summary.txt: overview system properties
- xmolout: .xyz coordinates

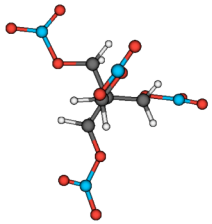



```
Bond order cutoff:0.3000
Iteration Freq. Molecular formula          Molecular mass
      0   1 x  C5H8O12N4                    316.0520
 Total number of molecules: 1
 Total number of atoms: 29
 Total system mass:  316.052
.........
.........
Iteration Freq. Molecular formula          Molecular mass
  40000   1 x  C5H8O10N3                    270.0540
  40000   1 x  O2N                         45.9980
 Total number of molecules: 2
 Total number of atoms: 29
 Total system mass:  316.052
```

molfra.out



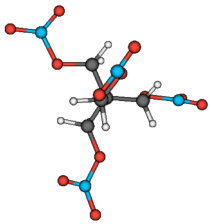
Single molecule simulations



PETN in 12.5x12.5x12.5 box
(PETN_minim)

Minimization

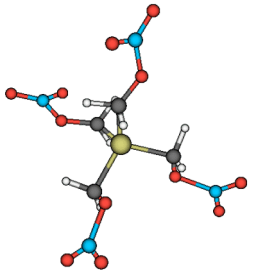
t_{cpu}<<1 sec.



Minimized PETN
(PETN_Si_minim)

Exchange
central C for Si

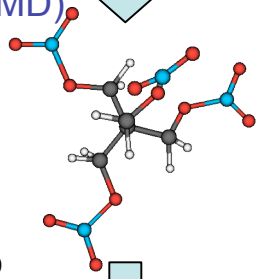
t_{cpu}<1 sec.



Minimized PETN_Si
(PETN_Si_minim)

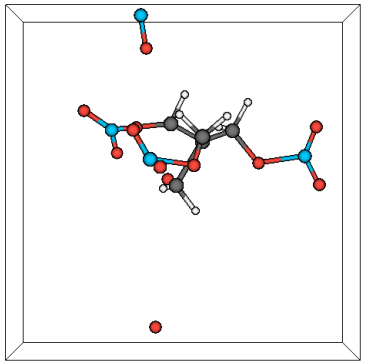
2.5 ps. MD at 300K
(PETN_300K_MD)

t_{cpu}-=85 sec.



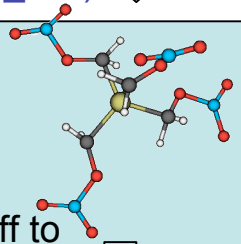
10 ps. MD-cookoff to
T=2000K
(PETN_cookoff)

t_{cpu}-=307 sec.



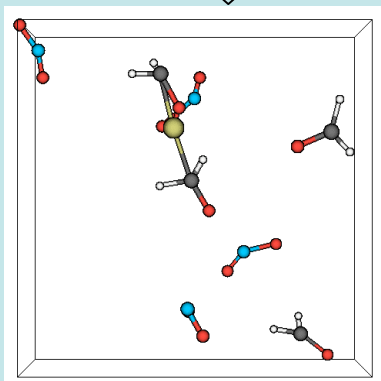
2.5 ps. MD at 300K
(PETN_Si_300K_MD)

t_{cpu}-=61 sec.



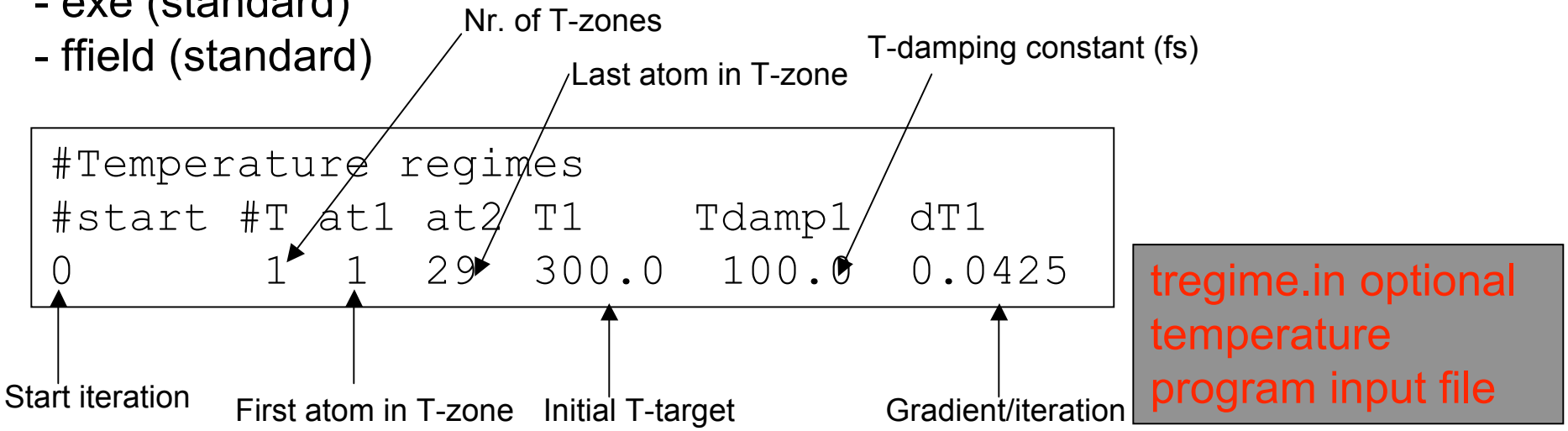
10 ps. MD-cookoff to
T=2000K
(PETN_Si_cookoff)

t_{cpu}-=213 sec



Input files

- tregime.in-file
- control-file (mdstep=40000, other keywords from PETN_Si_300K_MD)
- vels-restart file (copied from moldyn.vel from PETN_Si_300K_MD)
- geo (copied from fort.90 from PETN_300K_MD)
- exe (standard)
- ffield (standard)

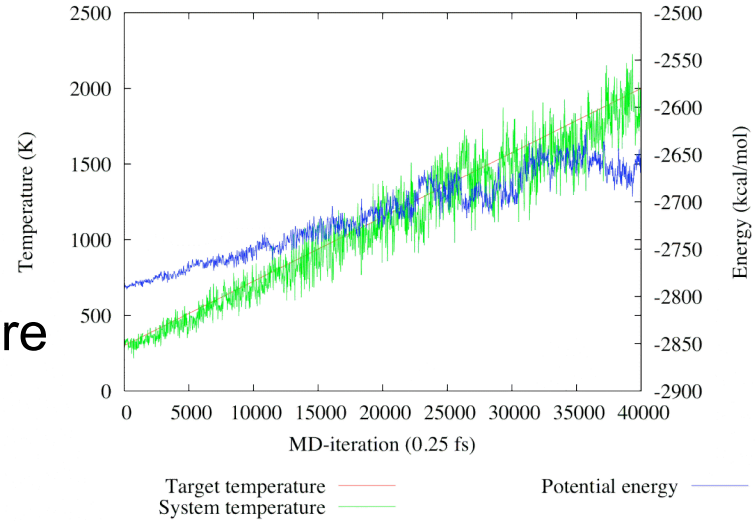


T_{target}(iteration 0) = 300K
T_{target}(iteration 40000) =2000K

Hierarchy: tregime.in-file overrides control-file

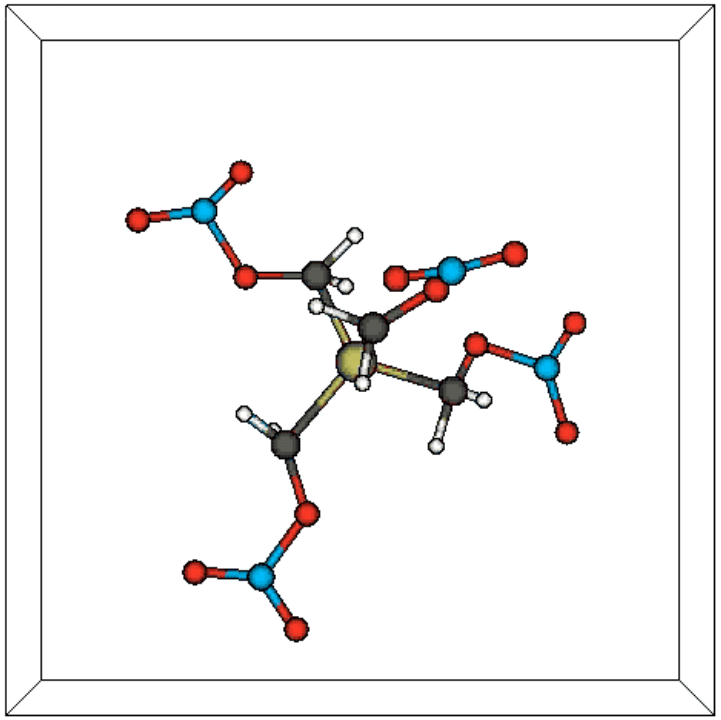
Output files

- fort.7, fort.8: connection table
- fort.71: energy, temperature data
- fort.73: final partial energies
- fort.75: overview target and system temperature
- fort.90: final geometry (.bgf)
- molfra.out : system composition
- moldyn.vel, molsav.####: restart-files
- summary.txt: overview system properties
- xmolout: .xyz coordinates

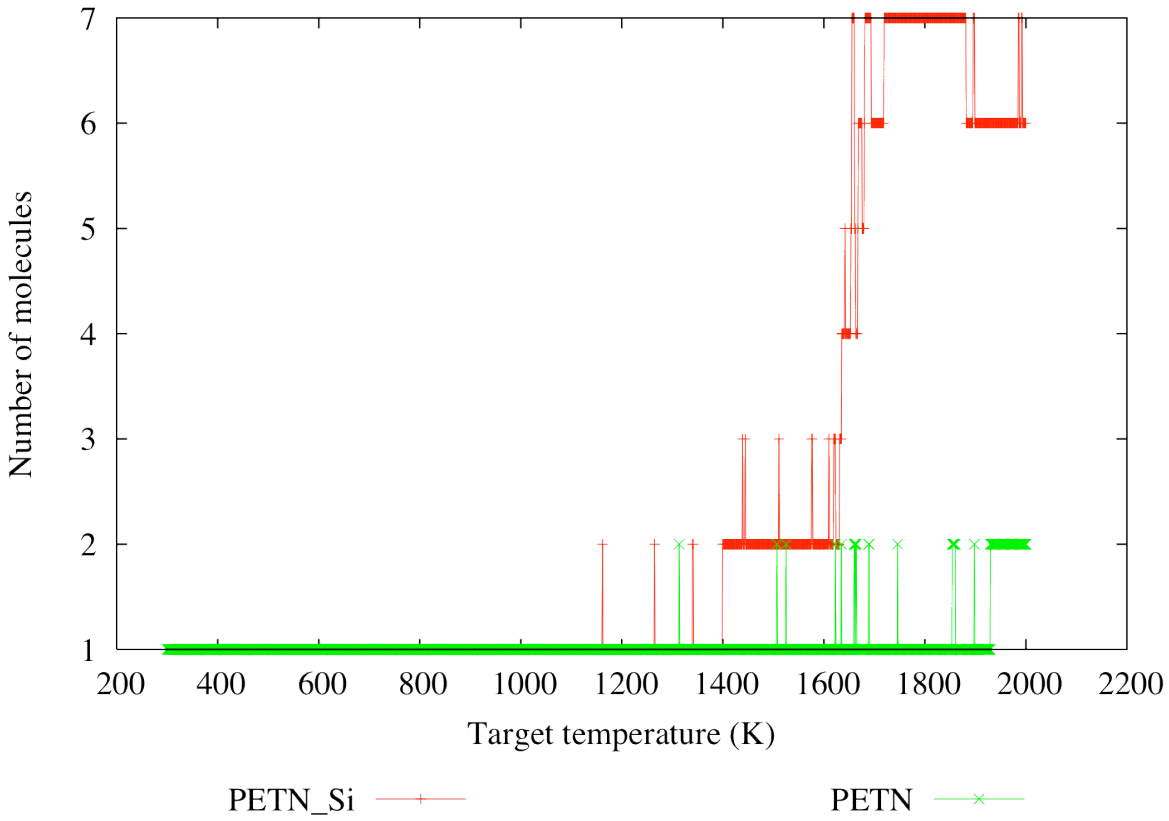



```
Bond order cutoff:0.3000
Iteration Freq. Molecular formula          Molecular mass
      0   1 x  C4H8O12N4Si                  332.1120
 Total number of molecules: 1
 Total number of atoms: 29
 Total system mass:  332.112
.........
.........
Iteration Freq. Molecular formula          Molecular mass
  40000   1 x  C2H4O4NSi                    134.0880
  40000   3 x  O2N                         45.9980
  40000   2 x  CH2O                        30.0150
 Total number of molecules: 6
 Total number of atoms: 29
 Total system mass:  332.112
```

molfra.out



Comparison PETN and PETN_Si



- PETN_Si is substantially more sensitive than PETN; this agrees with experimental findings from the Klapoetke-group (JACS 2007, **129**, 6908-6915)

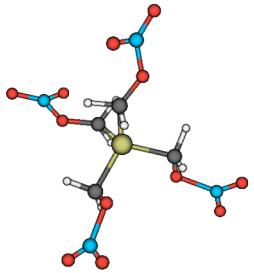
Examples

-Single molecules:
- minimization
- MD
- cookoff

-Periodic molecular systems:
- building
- compression
- piston simulations

-Combined molecular/condensed systems
-building
- MD

Periodic molecular systems

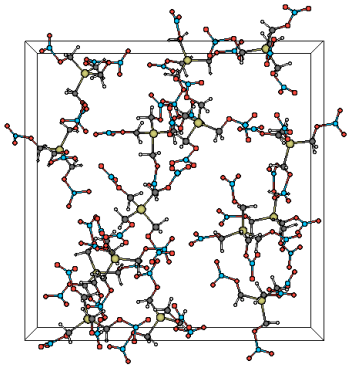


PETN_Si
(PETN_minim)

Duplicate with
place2-program

t_{cpu}<<1 sec.

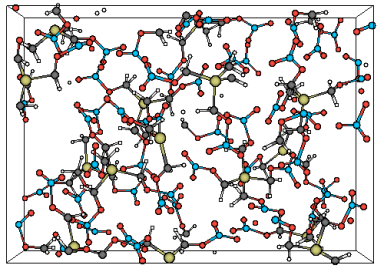
(place2/PETN_Si_box)



15 PETN_Si in 25x25x25 box
(15_PETN_Si)

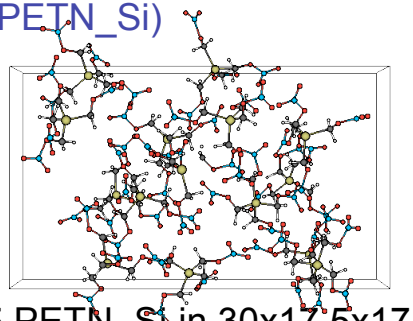
Compress in y
and z directions
at T=300K

t_{cpu}=858 sec.



15 PETN_Si in 25x17.5x17.5 box
(compress)

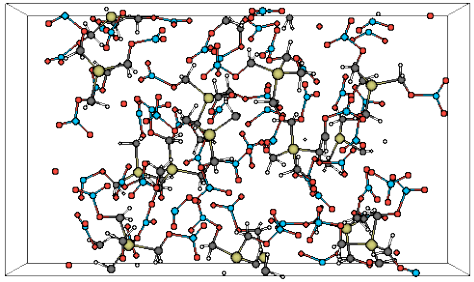
Reconstruct
molecules in x-
direction



15 PETN_Si in 30x17.5x17.5
box; no molecules crossing the
x-periodic boundary
(reconstruct)

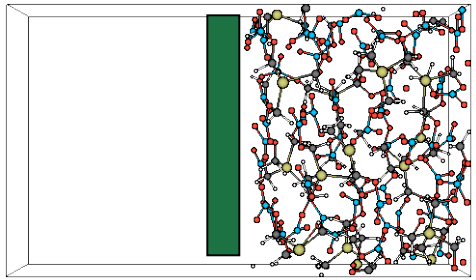
Equilibrate at T=300K with
reflective x-boundary

t_{cpu}=449 sec.



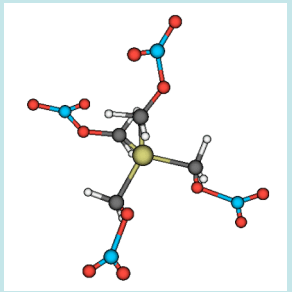
15 PETN_Si in 30x17.5x17.5
at T=300K
(reconstruct_300K_MD)

NVE-simulation
with moving piston
t_{cpu}=3500 sec.



Compressed 15 PETN_Si
(piston)

Periodic molecular systems

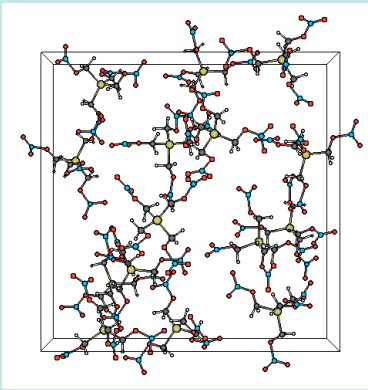


PETN_Si
(PETN_minim)

Duplicate with
place2-program

t_{cpu}<<1 sec.

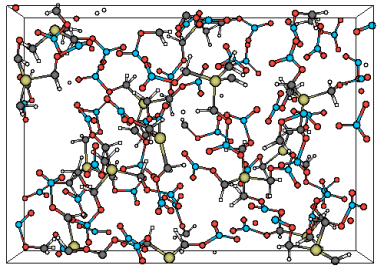
(place2/PETN_Si_box)



15 PETN_Si in 25x25x25 box
(15_PETN_Si)

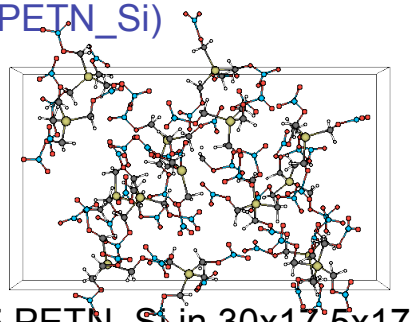
Compress in y
and z directions
at T=300K

t_{cpu}=858 sec.



15 PETN_Si in 25x17.5x17.5 box
(compress)

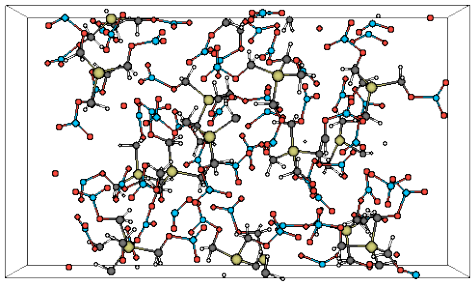
Reconstruct
molecules in x-
direction



15 PETN_Si in 30x17.5x17.5
box; no molecules crossing the
x-periodic boundary
(reconstruct)

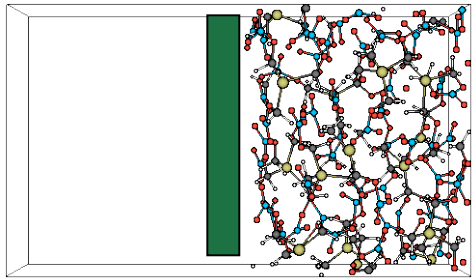
Equilibrate at T=300K with
reflective x-boundary

t_{cpu}=449 sec.



15 PETN_Si in 30x17.5x17.5
at T=300K
(reconstruct_300K_MD)

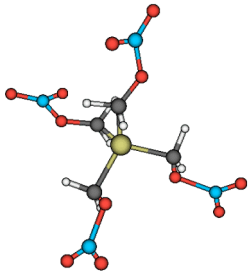
NVE-simulation
with moving piston
t_{cpu}=3500 sec.



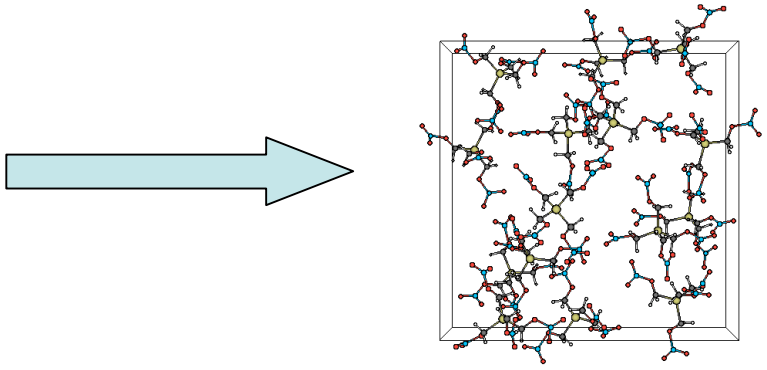
Compressed 15 PETN_Si
(piston)

Duplicating molecules with the place2-program

Input-files for place2: - geo (last xmolout-frame from PETN_Si_minim)
- control-file for place2 (see below)



PETN-Si



15 PETN-Si in 25x25x25 box; ρ=0.529 kg/dm^3

```
 15          ! Number of duplicates molecule to be put in periodic box
25.00000       ! Unit cell parameter a1 of periodic box  (Angstrom)
25.00000       ! Unit cell parameter b1 of periodic box (Angstrom)
25.00000       ! Unit cell parameter c1 of periodic box (Angstrom)
 90.00         ! Unit cell parameter alfa of periodic box
 90.00         ! Unit cell parameter beta of periodic box
 90.00         ! Unit cell parameter gamma of periodic box
 2.25          ! Minimum distance between molecules allowed (Angstrom)
  0            ! Read in (1) from geo2 set of molecules (cartesian coordinate
  1            ! (0) leave geo2-structure were it is (1) put geo2-structure in centre box (2) put geo2-structure at origin
50000          ! Number of non-succesful random placement steps allowed; aft
 1553          ! Seed for random generator
```

control-file for place2

-Run the place2-program (./place2 &)
- Follow progress in run.log; if placing takes to long kill program and change input parameters
- Output file: output.xyz; convert to .bgf with xtob:

Place2 cannot generate high-density systems.

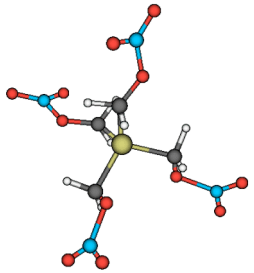
Converting .xyz to .bgf with xtob-script

```
>xtob
 Input file in .xyz-format ?
output.xyz
 Do you want to input cell parameters (y/n) ?
y
 x  y  z dimensions periodic box in Angstrom
25.0 25.0 25.0
 a  b  c angles periodic box in degrees
90.0 90.0 90.0
 Choose an option:
 0: do not sort
 1: sort by x-coordinate
 2: sort by y-coordinate
 3: sort by z-coordinate
 Which option (0-3)
0
STOP Normal end of program; output .bgf-file in fort,15 statement executed
>
```

Red text: program response

- Add system name to DESCRP-line (15_PETN_Si)
- Energy minimize the system; directory 15_PETN_Si

Periodic molecular systems

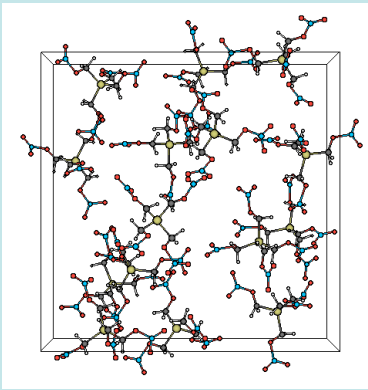


PETN_Si
(PETN_minim)

Duplicate with
place2-program

t_{cpu}<<1 sec.

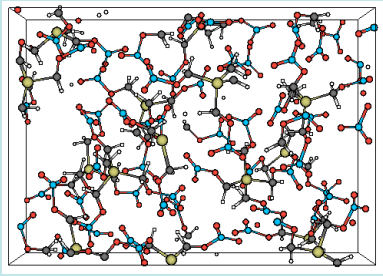
(place2/PETN_Si_box)



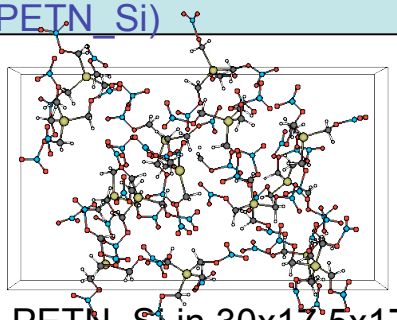
15 PETN_Si in 25x25x25 box
(15_PETN_Si)

Compress in y
and z directions
at T=300K

t_{cpu}=858 sec.



15 PETN_Si in 25x17.5x17.5 box
(compress)

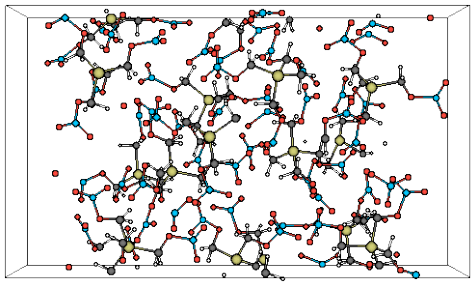


15 PETN_Si in 30x17.5x17.5
box; no molecules crossing the
x-periodic boundary
(reconstruct)

Reconstruct
molecules in x-
direction

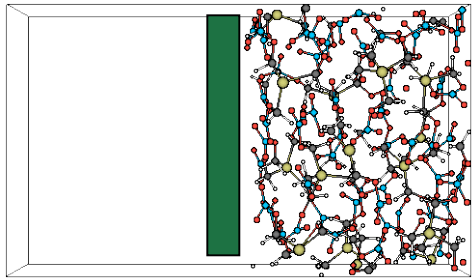
Equilibrate at T=300K with
reflective x-boundary

t_{cpu}=449 sec.



15 PETN_Si in 30x17.5x17.5
at T=300K
(reconstruct_300K_MD)

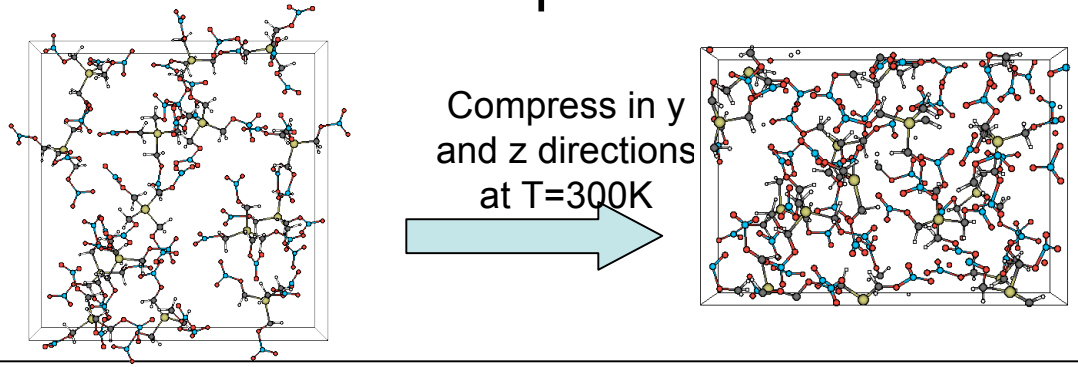
NVE-simulation
with moving piston
t_{cpu}=3500 sec.



Compressed 15 PETN_Si
(piston)

Compressing the system with the vregime.in

Input files




```
#Volume regimes
#start #V type1 change/it rescale type 2  change/it  rescale
0000    2  b  -0.003        y       c    -0.003        y
2500    2  b   0.000        y       c     0.000        y
```

vregime.in
optional
volume
control

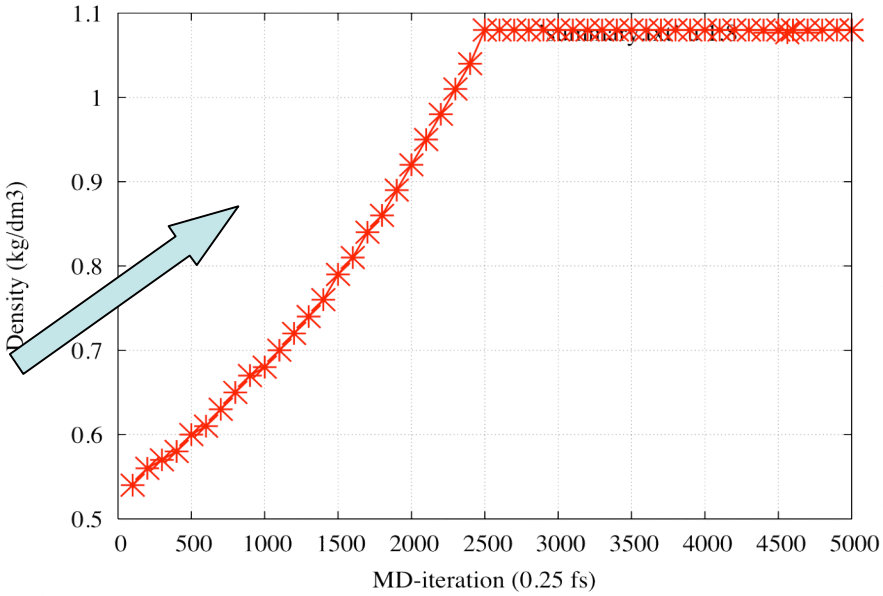
Iterations 0-2500: take b- and c-cell parameters from 25 Å to 17.5 Å (-0.003 Å/iteration)
Iterations 2500-5000: equilibrate the system at its new density (1.08 kg/dm^3)

Other input files:
- exe, ffield (standard)
- geo (fort.90 from 15_PETN_Si)
- control: defines 300K MD-simulation for 5000 iterations

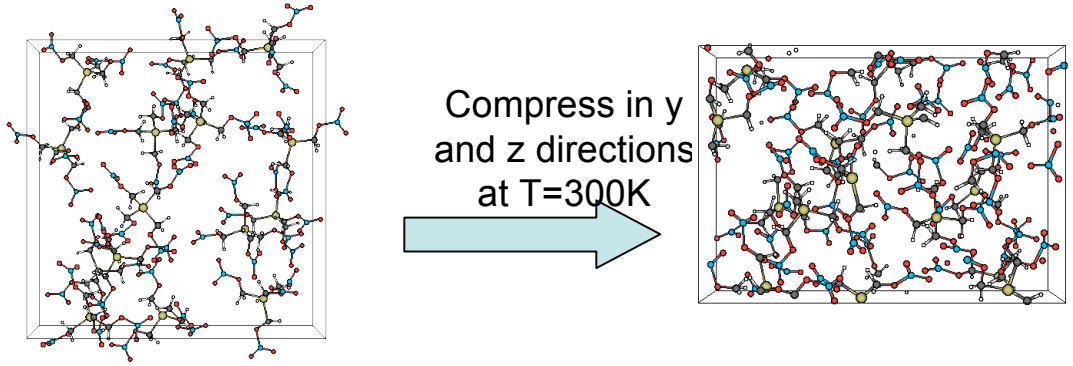
Compressing the system with the vregime.in

Output files

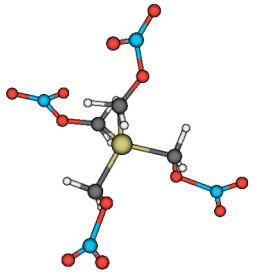
- fort.7, fort.8: connection table
- fort.71: energy, temperature data
- fort.73: final partial energies
- **fort.77: overview volume control**
- fort.90: final geometry (.bgf)
- molfra.out : system composition
- moldyn.vel, molsav.####: restart-files
- summary.txt: overview system properties
- xmolout: .xyz coordinates



Iterations 0-2500: take b- and c-cell parameters from 25 Å to 17.5 Å (-0.003 Å/iteration)
Iterations 2500-5000: equilibrate the system at its new density (1.08 kg/dm^3)



Periodic molecular systems

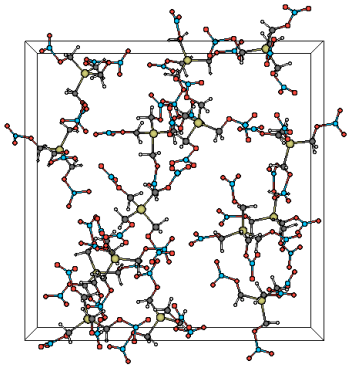


PETN_Si
(PETN_minim)

Duplicate with
place2-program

t_{cpu}<<1 sec.

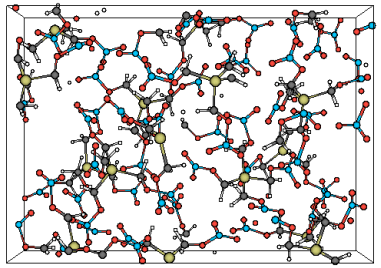
(place2/PETN_Si_box)



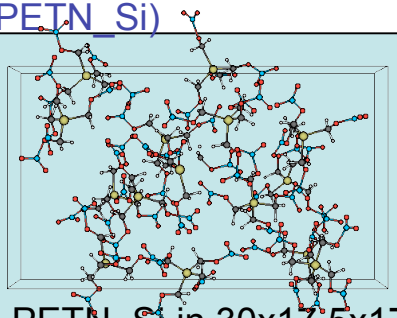
15 PETN_Si in 25x25x25 box
(15_PETN_Si)

Compress in y
and z directions
at T=300K

t_{cpu}=858 sec.



15 PETN_Si in 25x17.5x17.5 box
(compress)

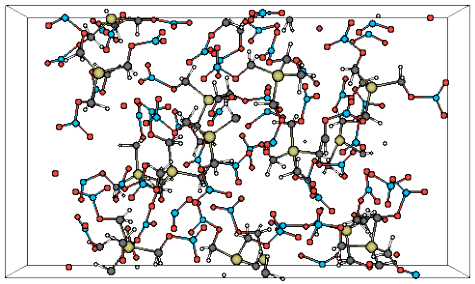


15 PETN_Si in 30x17.5x17.5
box; no molecules crossing the
x-periodic boundary
(reconstruct)

Reconstruct
molecules in x-
direction

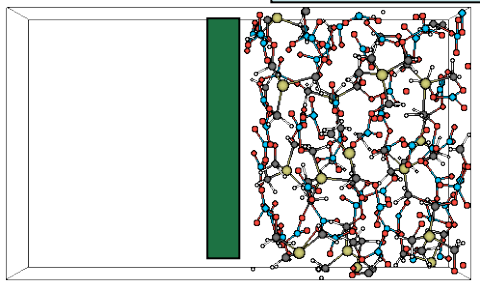
Equilibrate at T=300K with
reflective x-boundary

t_{cpu}=449 sec.



15 PETN_Si in 30x17.5x17.5
at T=300K
(reconstruct_300K_MD)

NVE-simulation
with moving piston
t_{cpu}=3500 sec.



Compressed 15 PETN_Si
(piston)

Preparing for the piston: 1) reconstruct molecules

- Take last frame from xmolout-file from compress/output

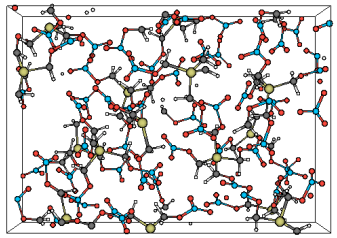
```
 435
15_PETN_Si    5000    -42157.54   25.00   17.50   17.50   90.00   90.00   90.00
Si   13.04657    0.56991    2.33189      1           6.30329
C    14.71106    0.55136    3.60987      1         -10.54045
.....
.....
O    22.15322    7.17524    5.35443     15          12.58712
O    19.96420    7.04840    5.29522     15           8.30073
```

xmolout

Molecule number (ixmolo=3, control-file)

Strain energy

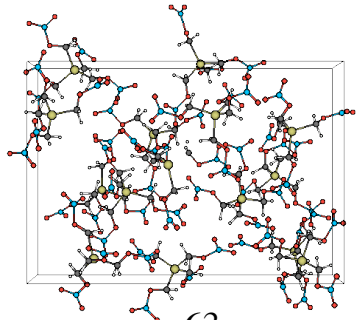
- Molecules cross all cell boundaries
- Need to clear these boundaries to introduce the piston



- Reconstruct the molecules using the xmolplaceback-script

```
> xmolplaceback
 Input file (xyz-format) ?
xmolout
 Cell parameters from input file (y/n) ?
y
 No offset (0);offset in x/y/z direction (1/2/3)
0
 Leave molecules (0); re-construct molecules (1)
1
 Which column holds molecule information (default 5) ?
5
 Normal end of program; output in fort.51
 Number of molecule reconstruction     iterations: 2
> mv fort.51 xmolout_placedback
```

Red text: program response

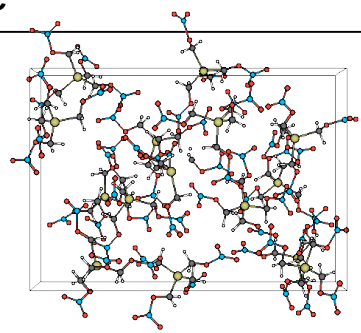


Preparing for the piston: 2) translate molecules

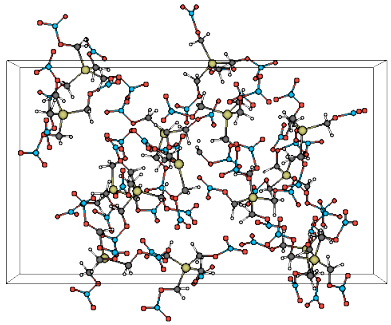
Shift all x-coordinates to remove all negative x-coordinates; extend a-axis by the same amount using xmolplaceback-script; this gives a 30 x 17.5 x 17.5 box with no molecules crossing the x-periodic boundary

```
> xmolplaceback
 Input file (xyz-format) ?
xmolout_placedback
 Cell parameters from input file (y/n) ?
n
 x y z dimensions periodic box
30 17.5 17.5
 a b c angles periodic box
90 90 90
 No offset (0);offset in x/y/z direction (1/2/3)
1
 Offset value
5.0
 Leave molecules (0); re-construct molecules (1)
1
 Which column holds molecule information (default 5) ?
5
 Normal end of program; output in fort.51
 Number of molecule reconstruction     iterations: 2
> mv fort.51 xmolout_placedback_shifted
```

- Molecules are reconstructed
- Some atoms have negative x-coordinates; need to shift these to positive

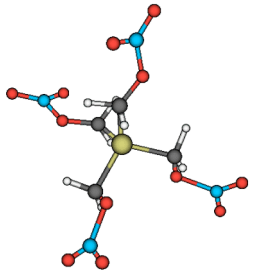


Red text: program response



- convert xmolplacedback_shifted to .bgf-input file using xtob

Periodic molecular systems

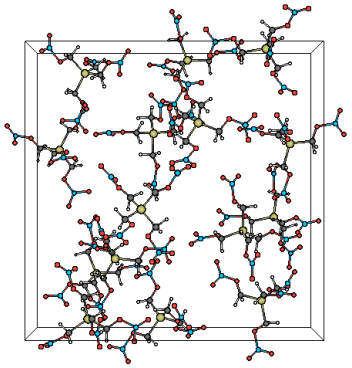


PETN_Si
(PETN_minim)

Duplicate with
place2-program

t_{cpu}<<1 sec.

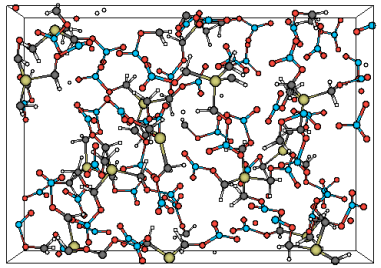
(place2/PETN_Si_box)



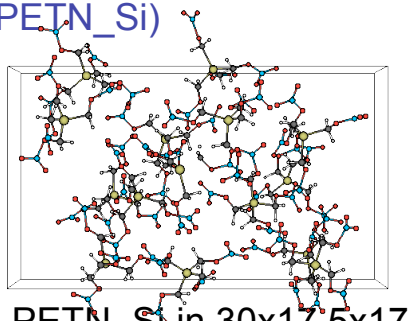
15 PETN_Si in 25x25x25 box
(15_PETN_Si)

Compress in y
and z directions
at T=300K

t_{cpu}=858 sec.

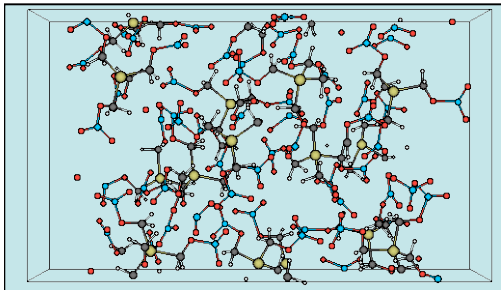


15 PETN_Si in 25x17.5x17.5 box
(compress)



15 PETN_Si in 30x17.5x17.5
box; no molecules crossing the
x-periodic boundary
(reconstruct)

Reconstruct
molecules in x-
direction

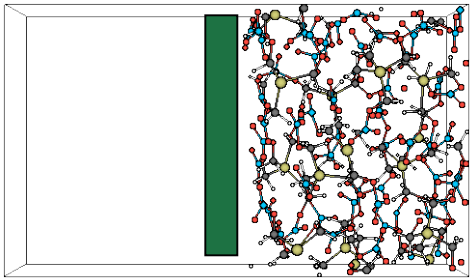


15 PETN_Si in 30x17.5x17.5
at T=300K
(reconstruct_300K_MD)

Equilibrate at T=300K with
reflective x-boundary

t_{cpu}=449 sec.

NVE-simulation
with moving piston
t_{cpu}=3500 sec.



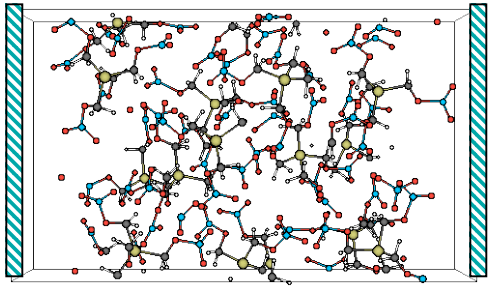
Compressed 15 PETN_Si
(piston)

Equilibrate reconstructed system with reflective x-boundary
Input files

```
# General parameters
      1 ireflx     1: reflective boundary in x-direction
      1 itrans     1: back translate atoms
      1 icentr
      0 imetho     0: Normal MD-run 1: Energy minimisation
      1 igeofo     0:xyz-input geometry 1: Biograf input
.........
      3 ixmolo     3: x,y,z+mol.nr.+Estrain
# MD-parameters
      1 imdmet     MD-method. 1:NVT/Berendsen thermostat
  0.250 tstep      MD-time step (fs)
0300.00 mdtemp     MD-temperature
0000.00 tincr      Increase/decrease temperature
      2 itdmet     0: T-damp atoms 1: Energy cons 2:System
  100.0 tdamp1     1st Berendsen/Anderson temperature damping
0000.00 mdpres     MD-pressure (MPa)
0002500 nmdit      Number of MD-iterations
  00001 ichupd     Charge update frequency
    010 iout1      Output to unit 71 and unit 73
   0100 iout2      Save coordinates
.........
      1 iravel     1: Random initial velocities
 001000 iout6      Save velocity file
 000025 irten      Frequency of removal
      0 npreit     Nr. of iterations in previous runs
  00.00 range      Range for back-translation of atoms
# MM-parameters
.......
```

control

- We should avoid molecules to drift back across the x-boundary during the simulation
- By using a reflective instead of a transparent x-boundary we avoid atoms hopping across
- y and z boundaries can be normally transparent

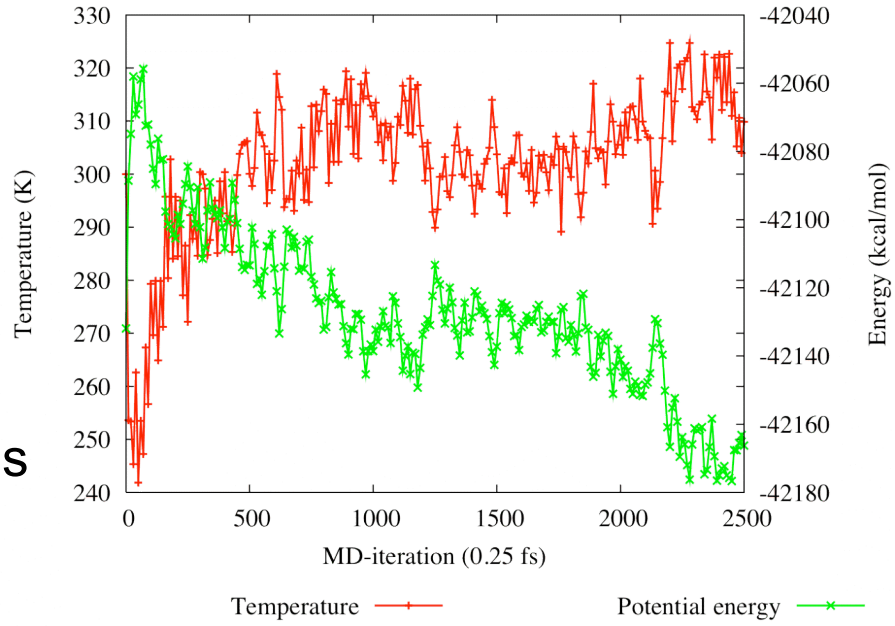


Other input files:
- exe, ffield (standard)
- geo (fort.15 from reconstruct)

Equilibrate reconstructed system with reflective x-boundary

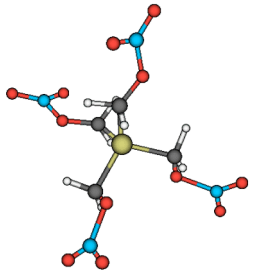
Output files

- fort.7, fort.8: connection table
- fort.71: energy, temperature data
- fort.73: final partial energies
- fort.90: final geometry (.bgf)
- molfra.out : system composition
- moldyn.vel, molsav.####: restart-files
- summary.txt: overview system properties
- xmolout: .xyz coordinates



- Temperature has equilibrated, energy not completely converged.

Periodic molecular systems

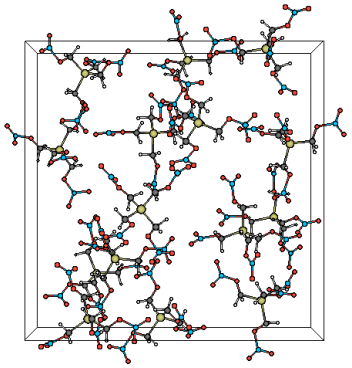


PETN_Si
(PETN_minim)

Duplicate with
place2-program

t_{cpu}<<1 sec.

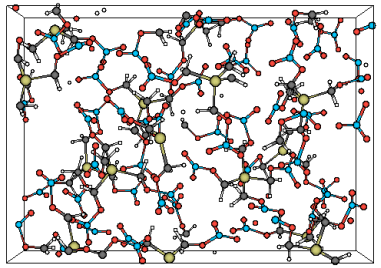
(place2/PETN_Si_box)



15 PETN_Si in 25x25x25 box
(15_PETN_Si)

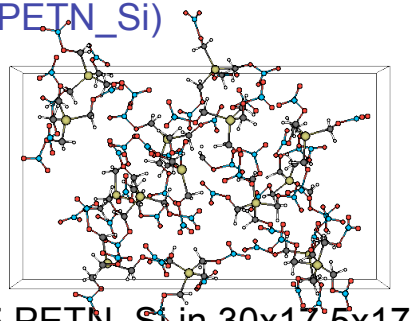
Compress in y
and z directions
at T=300K

t_{cpu}=858 sec.



15 PETN_Si in 25x17.5x17.5 box
(compress)

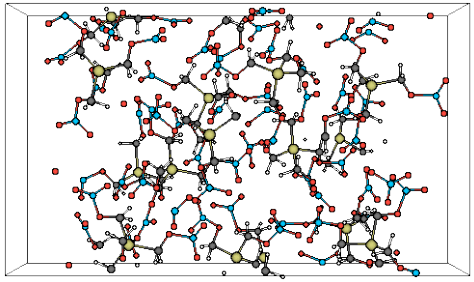
Reconstruct
molecules in x-
direction



15 PETN_Si in 30x17.5x17.5
box; no molecules crossing the
x-periodic boundary
(reconstruct)

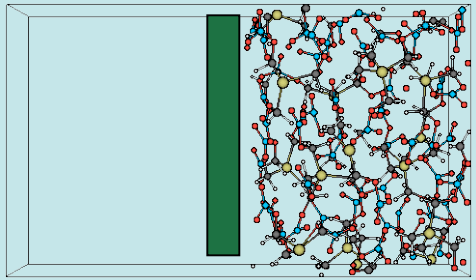
Equilibrate at T=300K with
reflective x-boundary

t_{cpu}=449 sec.



15 PETN_Si in 30x17.5x17.5
at T=300K
(reconstruct_300K_MD)

NVE-simulation
with moving piston
t_{cpu}=3500 sec.

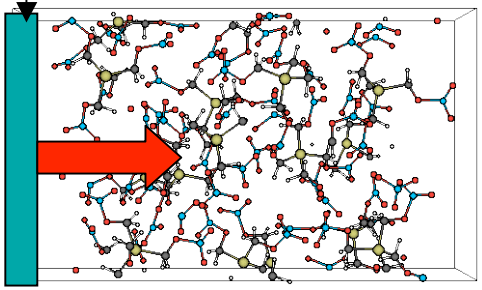


Compressed 15 PETN_Si
(piston)

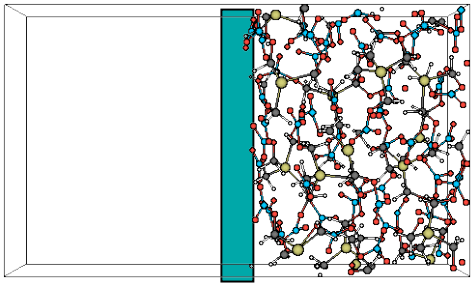
NVE-simulation with piston

Input files

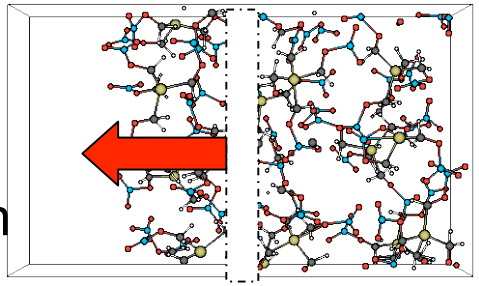
Piston



Iteration 0



Iteration 7500



Iterations 7500-20000: piston removed; system expands

x=0 x=15.00 x=30

Piston width

Piston direction

Piston centre start location

```
#piston regimes
#start  direction  Edeep1 Rdeep1  pshft1  Rcut1 speed1
0           x       0250.0  1.0    0.00    1.0   0.0020
7500        x       0000.0  1.0   15.00    1.0   0.000
```

Iteration

Piston potential

Piston speed (Å/iter)

piston.in
optional piston definitions

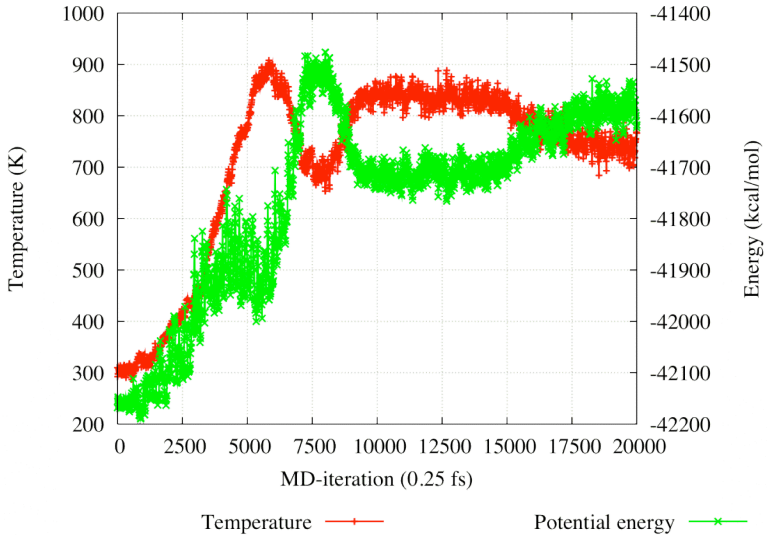
-Need to retain reflective x-boundary
- NVE simulation: allow system to heat up naturally

```
# General parameters
      1 ireflx      1: reflective boundary
                     in x-direction
……
# MD-parameters
      3 imdmet      MD-method. 3:NVE
  0.250 tstep       MD-time step (fs)
……
0020000 nmdit       Number of MD-iterations
……
```

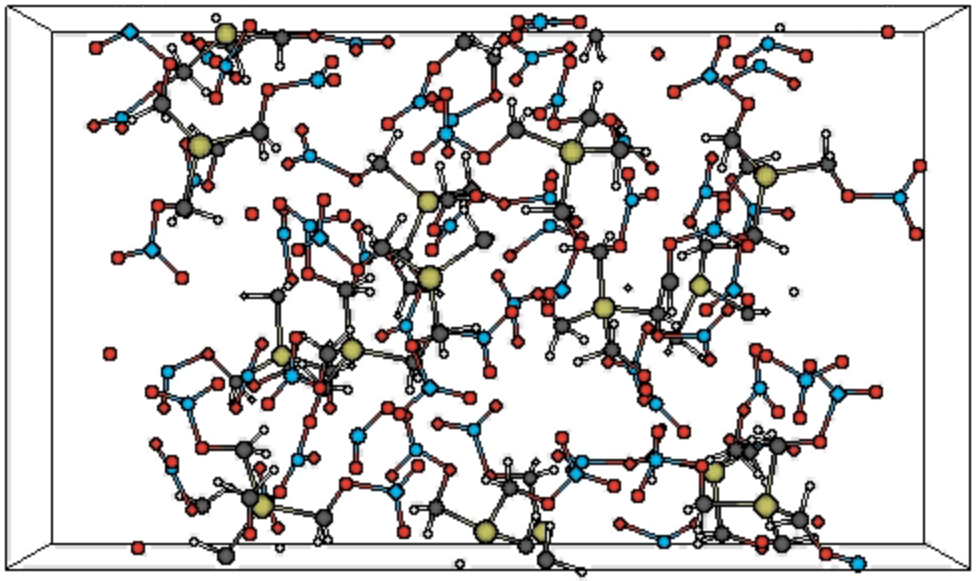
control

NVE-simulation with piston
Output files

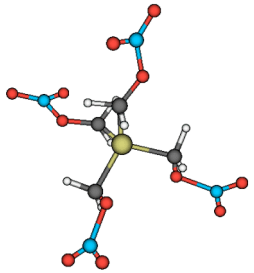
- fort.7, fort.8: connection table
- fort.71: energy, temperature data
- fort.73: final partial energies
- **fort.79: overview piston statistics**
- fort.90: final geometry (.bgf)
- molfra.out : system composition
- moldyn.vel, molsav.####: restart-files
- summary.txt: overview system properties
- xmolout: .xyz coordinates



- Potential energy reaches maximum at iteration 7500 (max compression)
- Energy release between iterations 7500-12500
- Reflective wave interference increases energy after iteration 15000
- No reactions



Periodic molecular systems

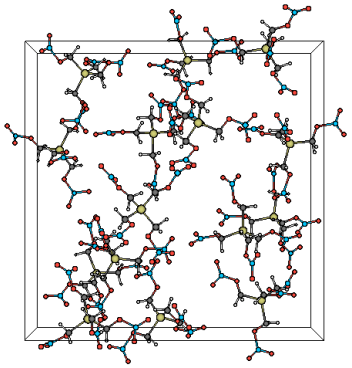


PETN_Si
(PETN_minim)

Duplicate with
place2-program

t_{cpu}<<1 sec.

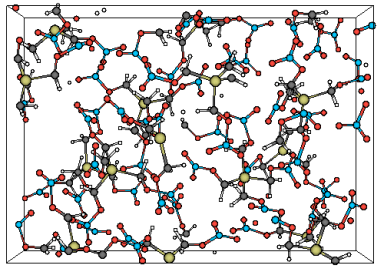
(place2/PETN_Si_box)



15 PETN_Si in 25x25x25 box
(15_PETN_Si)

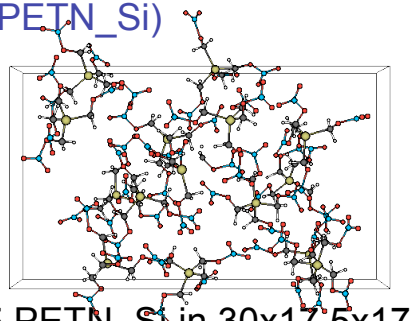
Compress in y
and z directions
at T=300K

t_{cpu}=858 sec.



15 PETN_Si in 25x17.5x17.5 box
(compress)

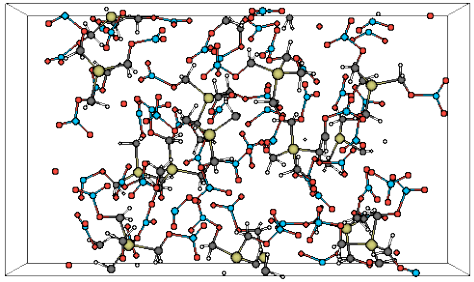
Reconstruct
molecules in x-
direction



15 PETN_Si in 30x17.5x17.5
box; no molecules crossing the
x-periodic boundary
(reconstruct)

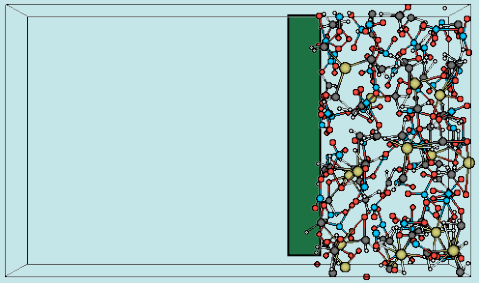
Equilibrate at T=300K with
reflective x-boundary

t_{cpu}=449 sec.



15 PETN_Si in 30x17.5x17.5
at T=300K
(reconstruct_300K_MD)

NVE-simulation with
faster moving piston
t_{cpu}=3500 sec.

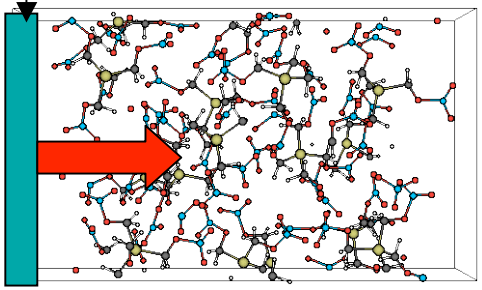


Highly compressed 15 PETN_Si
(fast_piston)

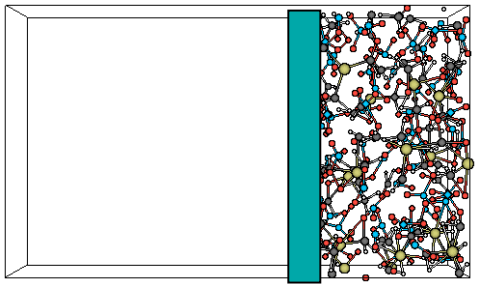
NVE-simulation with faster piston

Input files

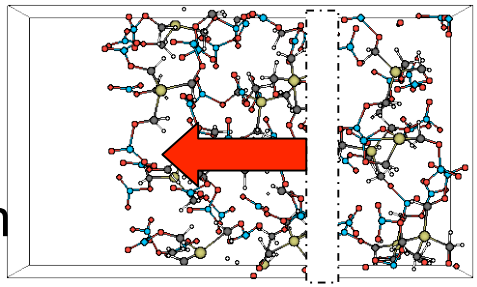
Piston



Iteration 0



Iteration 7500



Iterations 7500-20000: piston removed; system expands

x=0 x=18.75 x=30

Piston width

Piston direction

Piston centre start location

```
#piston regimes
#start  direction  Edeep1 Rdeep1  pshft1  Rcut1 speed1
0           x       0250.0  1.0     0.00    1.0   0.0025
7500        x       0000.0  1.0    17.50    1.0   0.000
```

Iteration

Piston potential

Piston speed (Å/iter)

piston.in optional piston definitions

-Need to retain reflective x-boundary
- NVE simulation: allow system to heat up naturally
- **Temperature will get >2000K; need smaller time step**

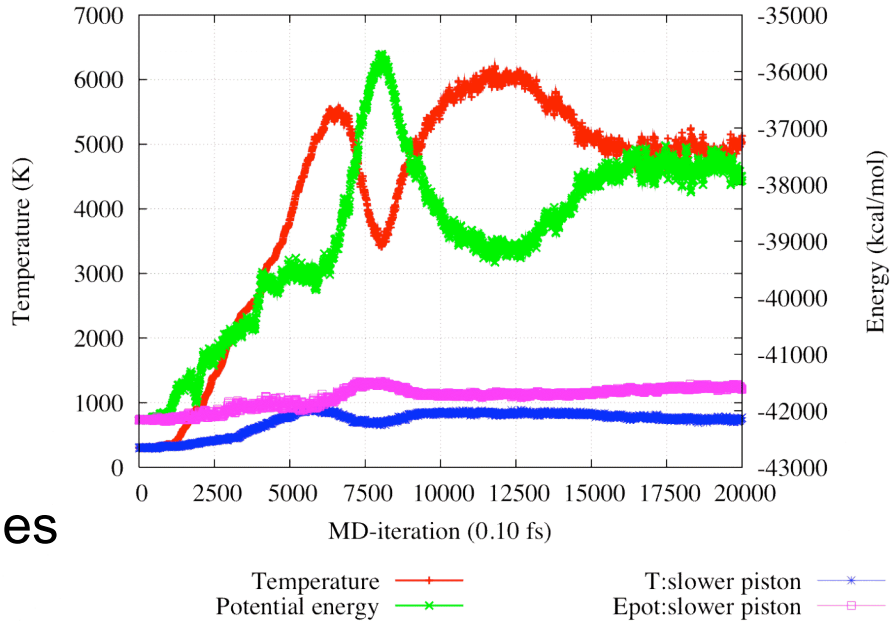
```
# General parameters
      1 ireflx      1: reflective boundary
                     in x-direction
……
# MD-parameters
      3 imdmet      MD-method. 3:NVE
  0.100 tstep       MD-time step (fs)
……
0020000 nmdit       Number of MD-iterations
……
```

control

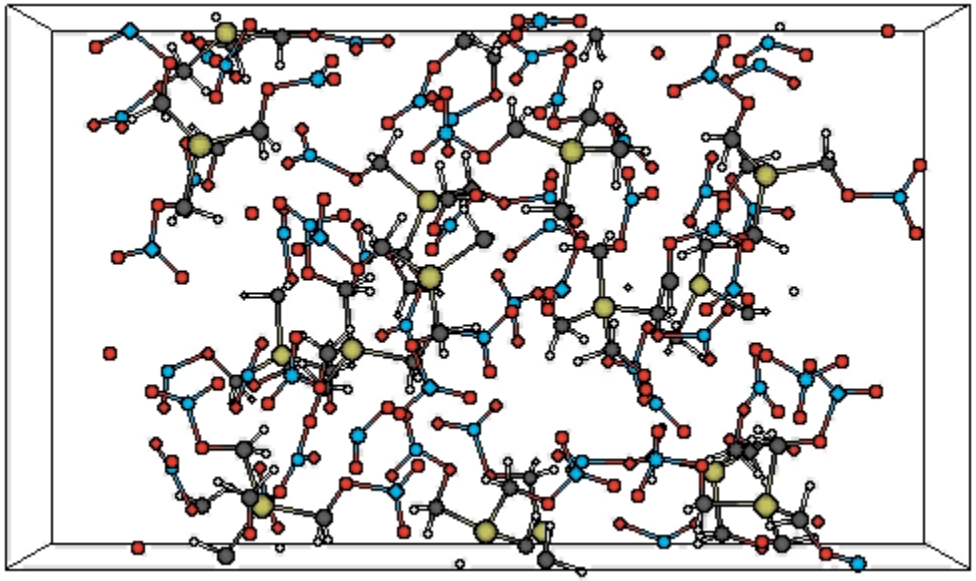
NVE-simulation with faster piston

Output files

- fort.7, fort.8: connection table
- fort.71: energy, temperature data
- fort.73: final partial energies
- **fort.79: overview piston statistics**
- fort.90: final geometry (.bgf)
- molfra.out : system composition
- moldyn.vel, molsav.####: restart-files
- summary.txt: overview system properties
- xmolout: .xyz coordinates



- Potential energy reaches maximum at iteration 7500 (max compression)
- Energy release between iterations 7500-12500
- Reflective wave interference increases energy after iteration 15000
- Substantial amount of reactions



NVE-simulation with faster piston

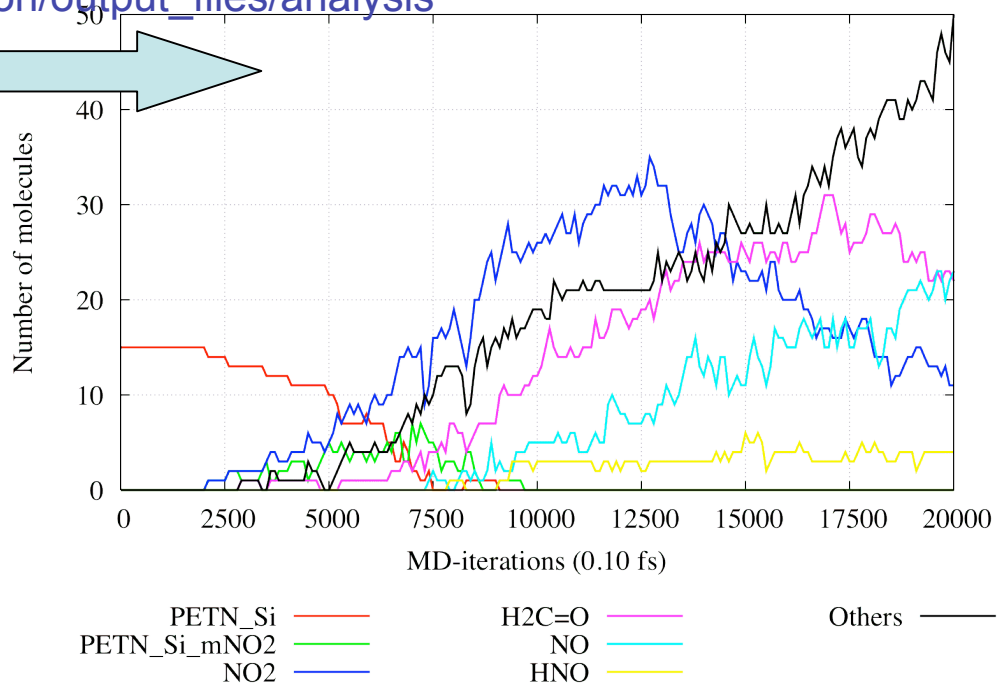
Plotting molecule fragments

molfraanal-script

fast_piston/output_files/analysis

```
Bond order cutoff:0.3000
Iteration Freq. Molecular formula            Molecular mass
       0  15 x  C4H8O12N4Si                    332.1120
 Total number of molecules:        15
 Total number of atoms:        435
 Total system mass:   4981.68000000000
Iteration Freq. Molecular formula            Molecular mass
     100  15 x  C4H8O12N4Si                    332.1120
 Total number of molecules:        15
 Total number of atoms:        435
 Total system mass:   4981.68000000000
Iteration Freq. Molecular formula            Molecular mass
     200  15 x  C4H8O12N4Si                    332.1120
 Total number of molecules:        15
 Total number of atoms:        435
 Total system mass:   4981.68000000000
.............
Iteration Freq. Molecular formula            Molecular mass
   20000   1 x  CH3O5Si2                       151.1390
   20000   3 x  CO2                          43.9980
   20000   1 x  C2H3O6NSi                      165.0780
   20000   4 x  HON                          31.0070
   20000   1 x  HO3N                         63.0050
   20000  23 x  ON                           29.9990
   20000   4 x  HO2N                         47.0060
   20000  22 x  CH2O                         30.0150
   20000   1 x  CH2O2Si                      74.0740
   20000   1 x  C4H8O10N2Si2                  300.1740
   20000   5 x  O2                         31.9980
   20000   1 x  C2H4O2Si                      88.0900
   20000  11 x  O2N                          45.9980.....
...............
...............
   20000   1 x  CH2O3N                       76.0130
   20000   1 x  CON                         41.9990
   20000   1 x  CO3                         59.9970
   20000   1 x  CH2O2N                       60.0140
   20000   1 x  CO                          27.9990
   20000   1 x  H                           1.0080
   20000   2 x  O                           15.9990
 Total number of molecules:       110
 Total number of atoms:        435
 Total system mass:   4981.68000000000
```

molfra.out: molecular fragment information



Red text: program response

```
> molfraanal
 Input file (probably molfra.out) ?
molfra.out
 Cutoff for compound frequency ?
5
STOP Normal end of program statement executed
```

- Output files (fr1.dat, mass1.dat) can be directly plotted

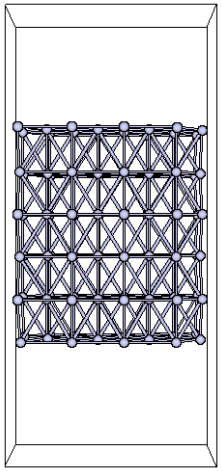
Examples

-Single molecules:
- minimization
- MD
- cookoff

-Periodic molecular systems:
- building
- compression
- piston simulations

-Combined molecular/condensed systems
- building
- MD

Combined molecular/condensed systems

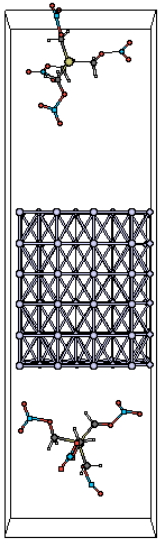


Al111-surface in
11.48x25x9.94 box

Add 2 PETN_Si
with place2

t_{cpu}<<1 sec.

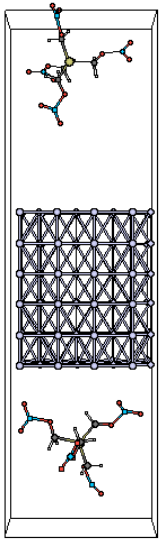
(place2/Al_surface_PETN)

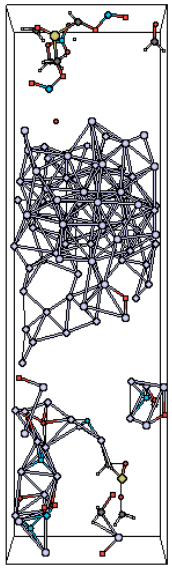


2 PETN_Si with Al[111] in 11.48x40x9.94 box
(Al111_2PETN_Si_minim)

Energy minimize

t_{cpu}=12 sec.

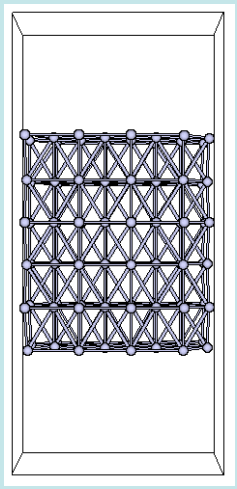




Molten and oxidized Al-phase

MD-simulation at T=1000K
Al111_2PETN_Si_1000K_MD

Combined molecular/condensed systems

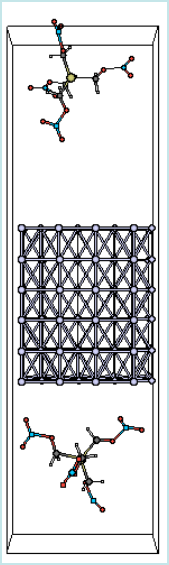


Al111-surface in
11.48x25x9.94 box

Add 2 PETN_Si
with place2

t_{cpu}<<1 sec.

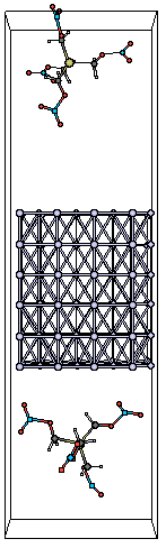
(place2/Al_surface_PETN)

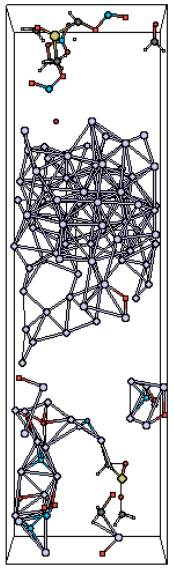


2 PETN_Si with Al[111] in 11.48x40x9.94 box

Energy minimize
Al111_2PETN_Si_minim

t_{cpu}=12 sec.



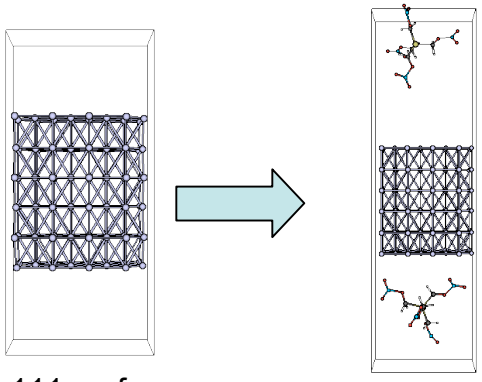


Molten and oxidized Al-phase

MD-simulation at T=1000K
Al111_2PETN_Si_1000K_MD

Adding molecules with the place2-program

Input-files for place2:
- geo (last xmolout-frame from PETN_Si_minim)
- geo2 (.xyz-structure with Al[111] surface)
- control-file for place2 (see below)



Al-111 surface

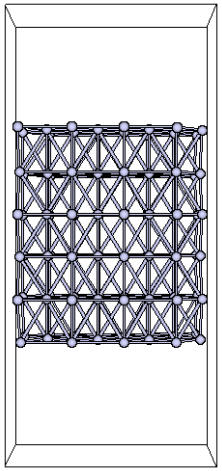
Al-111 surface with 2 PETN_Si

```
 2             ! Number of duplicates molecule to be put in periodic box
11.48000         ! Unit cell parameter a1 of periodic box  (Angstrom)
40.00000          ! Unit cell parameter b1 of periodic box (Angstrom)
 9.94000        ! Unit cell parameter c1 of periodic box (Angstrom)
 90.00          ! Unit cell parameter alfa of periodic box
 90.00          ! Unit cell parameter beta of periodic box
 90.00          ! Unit cell parameter gamma of periodic box
 3.00           ! Minimum distance between molecules allowed (Angstrom)
  1             ! Read in (1) from geo2 set of molecules (cartesian coordinate)
  1             ! (1) put geo2-structure in centre box
50000           ! Number of non-succesful random placement steps allowed; aft
 1553           ! Seed for random generator
```

control-file for place2

- Run the place2-program (./place2 &)
- Follow progress in run.log; if placing takes to long kill program and change input parameters
- Output file: output.xyz; convert to .bgf with xtob:

Combined molecular/condensed systems

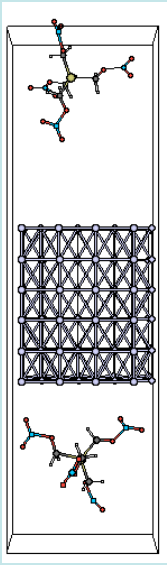


Al111-surface in
11.48x25x9.94 box

Add 2 PETN_Si
with place2

t_{cpu}<<1 sec.

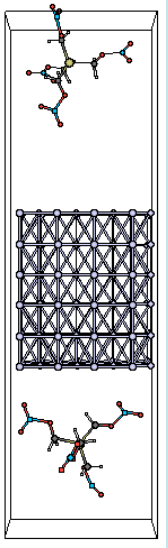
(place2/Al_surface_PETN)

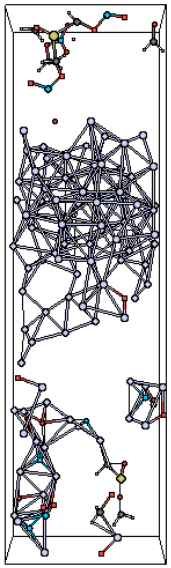


2 PETN_Si with Al[111] in 11.48x40x9.94 box

Energy minimize
Al111_2PETN_Si_minim

t_{cpu}=12 sec.





Molten and oxidized Al-phase

MD-simulation at T=1000K
Al111_2PETN_Si_1000K_MD

Input files

- exe (standard)
- control (standard)
- geo (fort.15 from place2/Al_surface_PETN)
- ffield (from trainingsets/Al_no_inner)

Overview force field files in trainingsets:
Al_no_inner: 2006 Al/nitramine potential; describes nitramines, Al/H//C/N/O and Si/C/O/H interactions
Si_PETN_inner: 2008 Si_PETN inner wall (under development)

Output files

Al111_2PETN_Si

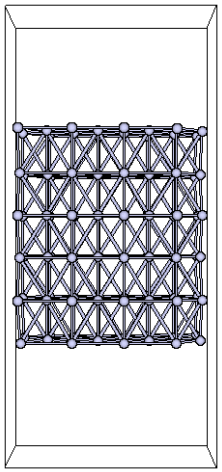
Iter.	Epot	Max.move	Factor	RMSG	nfc
0	-13466.5179186069	0.000000	0.500000	16.248083	0
1	-13478.4152551214	124.519814	8.284203	3.681996	0
2	-13481.3487254877	27.456306	0.112894	5.146173	0
3	-13487.7889777370	0.003283	5.982329	3.226126	0
4	-13488.9190466175	0.004498	1.426257	2.671802	0
5	-13493.0767197127	0.006679	4.350999	4.572713	0
6	-13495.7438630840	0.011106	1.800558	2.573608	0
7	-13496.6648441713	0.008690	0.866185	2.239404	0
8	-13497.8647262538	0.005993	2.154784	2.497644	0
9	-13498.5990084313	0.005683	1.631781	1.664182	0
10	-13498.9317308337	0.004304	1.112152	1.485149	0
…….					
38	-13518.0302882877	0.013764	1.674598	1.046043	0
39	-13518.1958614259	0.005974	1.877127	1.078181	0
40	-13518.5516823865	0.006998	2.333051	1.545835	0
41	-13518.8329564707	0.008684	1.489127	1.237245	0
42	-13519.1629438779	0.007401	2.186980	1.429959	0
43	-13519.4234414821	0.009701	1.656464	1.308842	0
44	-13519.6499359918	0.010981	1.253426	0.981372	0

Minimization report

fort.57

Other output files:
- fort.7, fort.8: connection table
- fort.58: partial energies
- fort.73: final partial energies
- fort.90: final geometry (.bgf)
- xmolout: .xyz coordinates
- molfra.out : system composition

Combined molecular/condensed systems

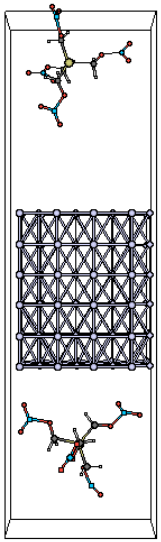


Al111-surface in
11.48x25x9.94 box

Add 2 PETN_Si
with place2

t_{cpu}<<1 sec.

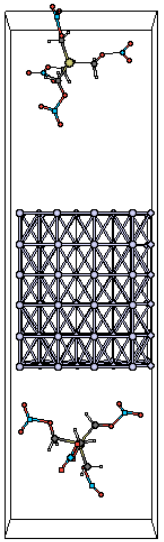
(place2/Al_surface_PETN)

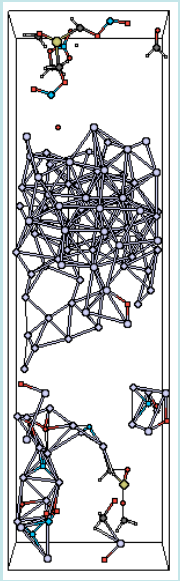


2 PETN_Si with Al[111] in 11.48x40x9.94 box

Energy minimize
Al111_2PETN_Si_minim

t_{cpu}=12 sec.





MD-simulation at T=1000K
Al111_2PETN_Si_1000K_MD

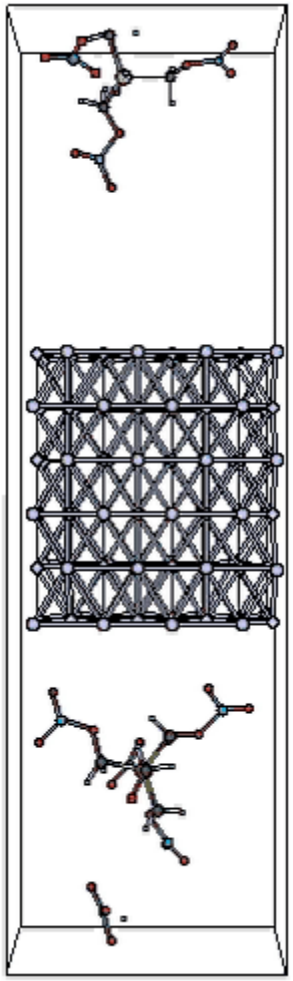
Molten and oxidized Al-phase

Input files

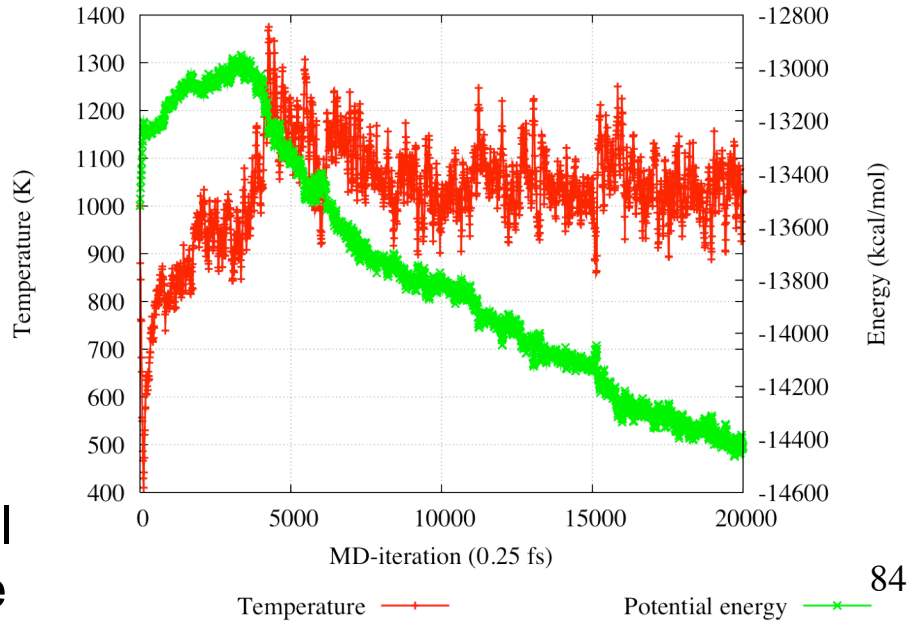
- exe (standard)
- control (standard)
- geo (fort.90 from Al111_2PETN_Si_minim)
- ffield (from trainingsets/Al_no_inner)

```
# General parameters
      1 itrans     0: do not back-translate atoms  1: back translate atoms
      1 icentr     0: keep position   1: put centre of mass in centre periodic cell
      0 imetho     0: Normal MD-run 1: Energy minimisation 2:MD-energy minimisation
      1 igeofo     0:xyz-input geometry 1: Biograf input geometry 2: xmol-input geometry
…….
      3 ixmolo     0: only x,y,z-coordinates in xmolout  3: x,y,z+mol.nr.+Estrain
# MD-parameters
      1 imdmet     MD-method. 1:NVT/Berendsen thermostat
  0.250 tstep      MD-time step (fs)
1000.00 mdtemp     MD-temperature
      2 itdmet     0: T-damp atoms 1: Energy cons 2:System
  100.0 tdamp1     1st Berendsen/Anderson temperature damping constant (fs)
…….
0020000 nmdit      Number of MD-iterations
  00001 ichupd     Charge update frequency
    010 iout1      Output to unit 71 and unit 73
   0100 iout2      Save coordinates
      0 ivels      1:Set vels and accels from moldyn.vel to zero
  00025 itrafr     Frequency of trarot-calls
      1 iout3      0: create moldyn.xxxx-files 1: do not create moldyn.xxxx-files
      1 iravel     1: Random initial velocities
 002500 iout6      Save velocity file
 000025 irten      Frequency of removal of rotational and translational energy
      0 npreit     Nr. of iterations in previous runs
  00.00 range      Range for back-translation of atoms
# MM-parameters
…….
```

Output files



- fort.7, fort.8: connection table
- fort.71: energy, temperature data
- fort.73: final partial energies
- fort.90: final geometry (.bgf)
- molfra.out : system composition
- moldyn.vel, molsav.####: restart-files
- summary.txt: overview system properties
- xmolout: .xyz coordinates



- Al-surface melts and becomes oxidizes; PETN_Si molecules fall apart; substantial energy release

Additional ReaxFF features

- Multiple thermostats
- Cell volume manipulation
- Electric field
- Distance, angle and torsion restraints
- Adding new molecules during MD-simulation

Multiple thermostats

tregime.in

#Temperature regimes

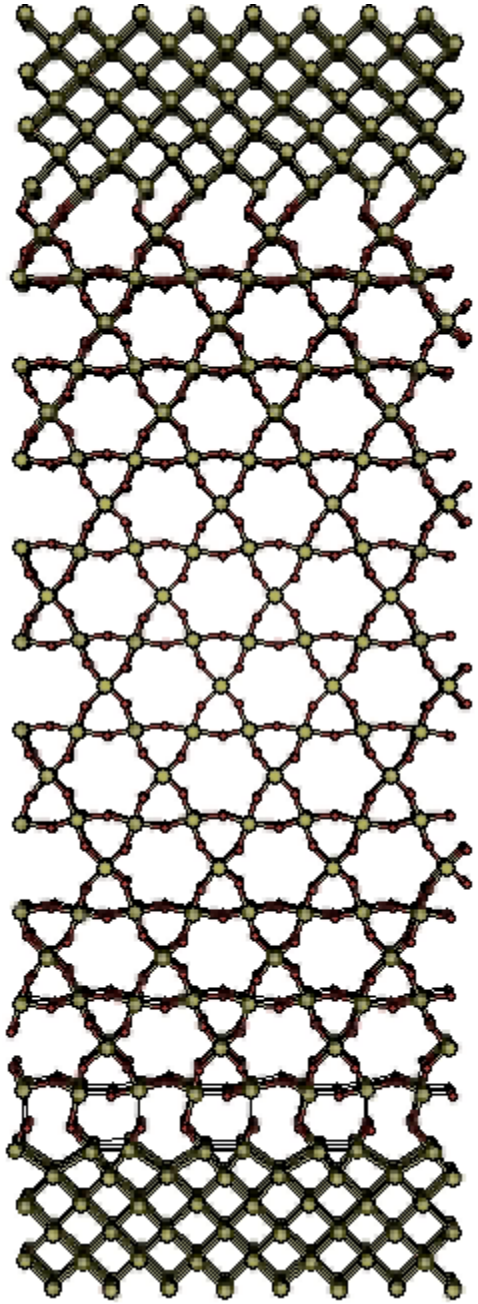
#start	#T	at1	at2	T1	Tdam1	dT1	at3	at4	T2	Tdam2	dT2
0	2	1	152	200.0	50.0	0.29	153	256	100.0	2.5	0.00
20000	2	1	152	6000.0	50.0	-0.29	153	256	100.0	2.5	0.00
40000	2	1	152	200.0	50.0	0.00	153	256	100.0	2.5	0.00

Start iteration of temperature program

Nr. of temperature zones in program

First temperature zone (first atom, last atom, temperature (K), temperature damping constant (fs), temperature increase/iteration

Second temperature zone (first atom, last atom, temperature (K), temperature damping constant (fs), temperature increase/iteration



Multiple thermostats

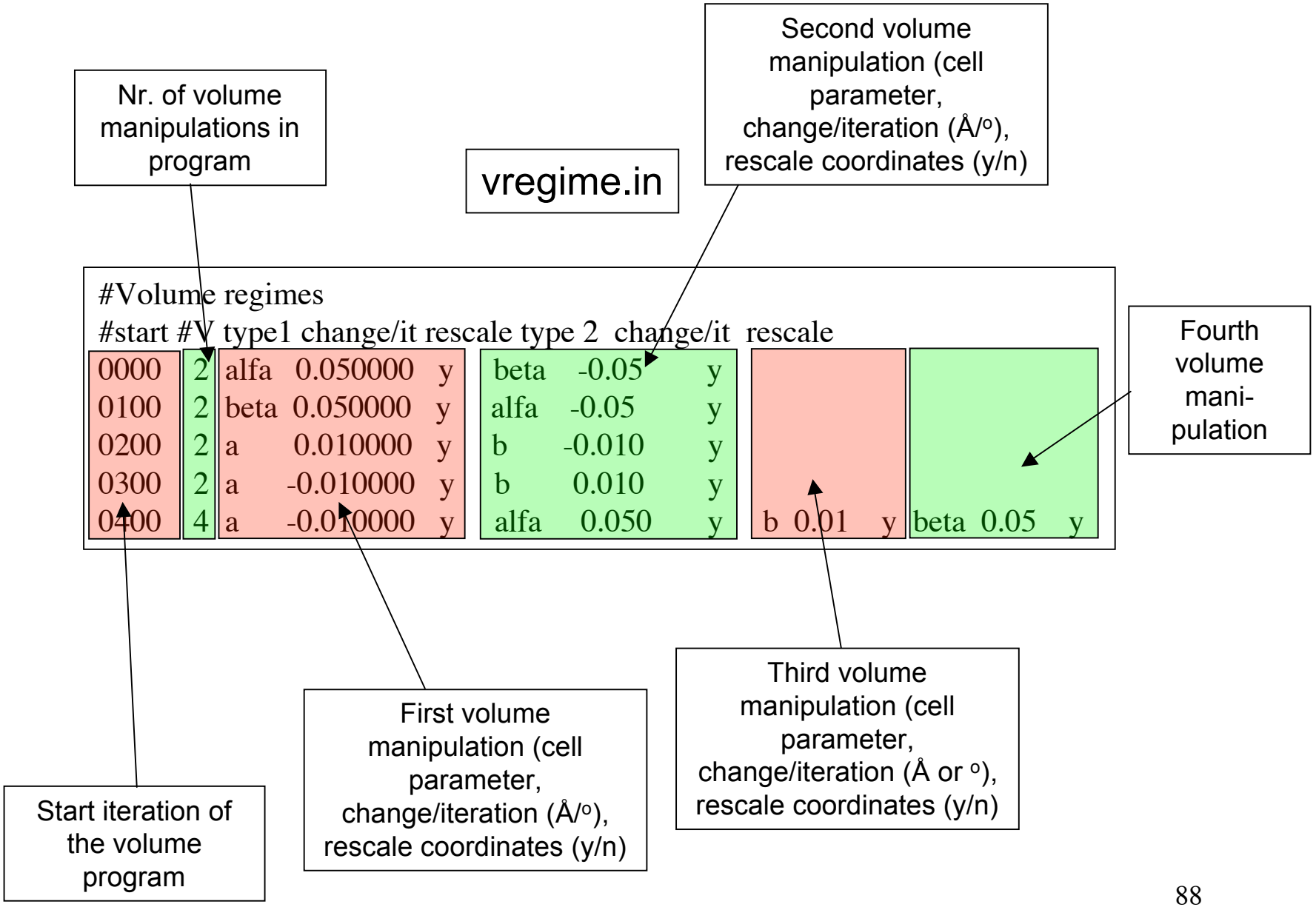
Example: Si/SiO_2 interface

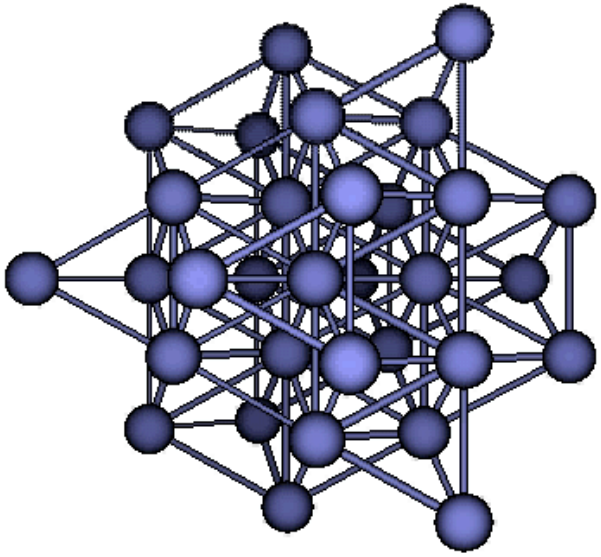
To generate an amorphous SiO_2/Si(alpha) 2 temperature zones are defined:

1) Si-phase: keep at 100K
2) SiO_2-phase: heatup from 200K to 6000K in 20,000 steps; keep at 6000K for 20,000 steps; cool back down to 200K in 20,000 steps

```
#Temperature regimes
#start  #T at1 at2 T1    Tdam1  dT1   at3 at4   T2   Tdam2 dT2
0        2  1 152  200.0   50.0  0.29 153 256 100.0  2.5 0.00
20000    2  1 152 6000.0   50.0 -0.29 153 256 100.0  2.5 0.00
40000    2  1 152  200.0   50.0  0.00 153 256 100.0  2.5 0.00
```

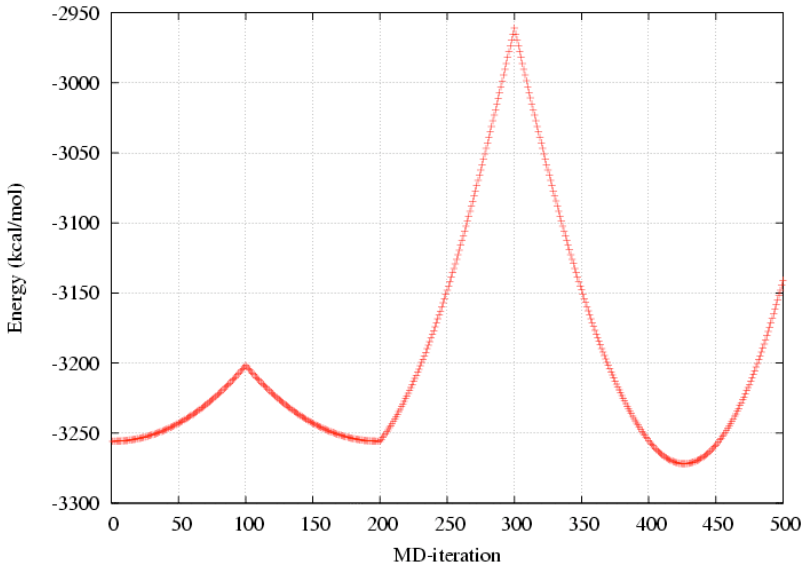
Cell volume manipulation





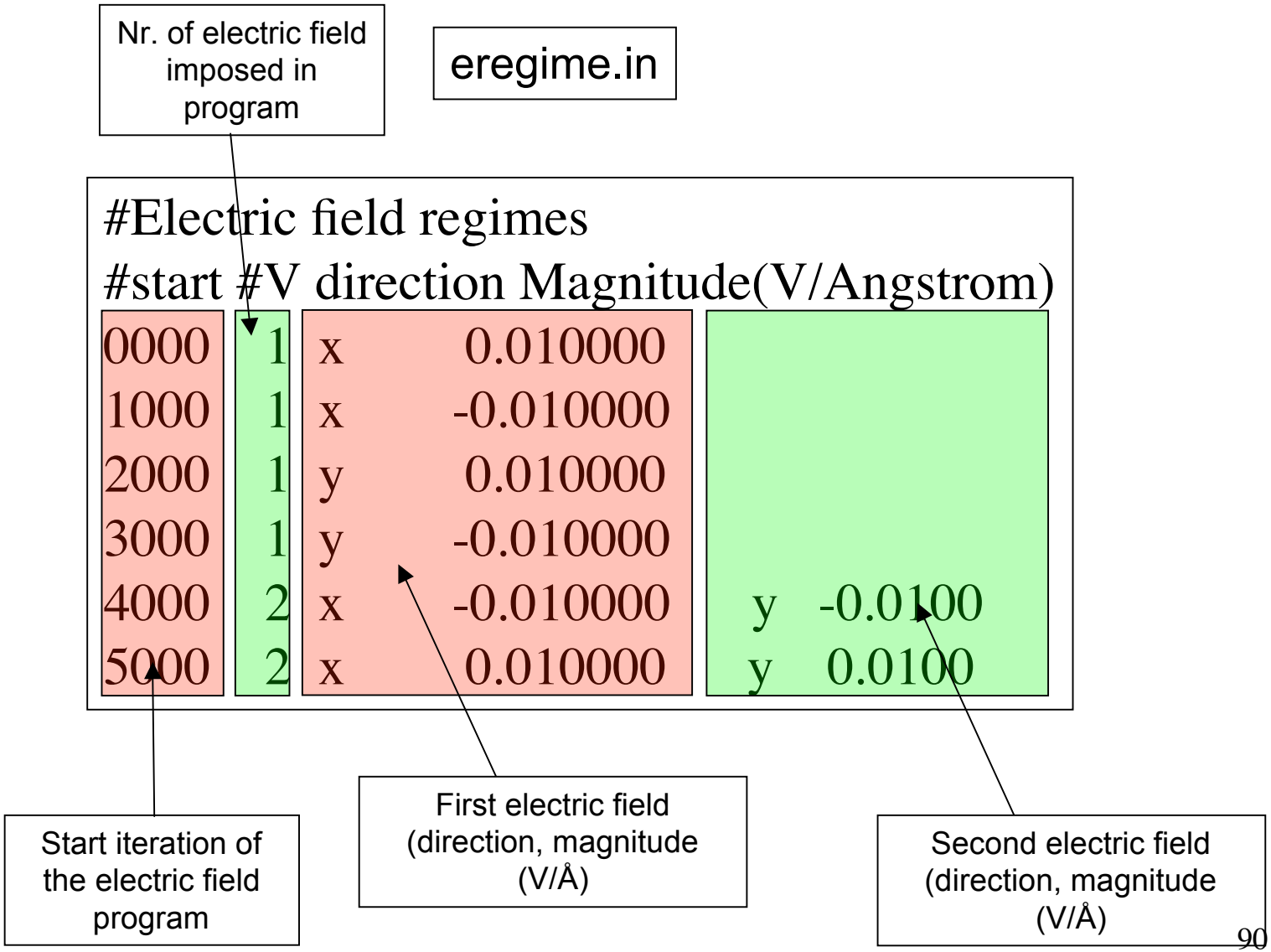
Example: 32 atom Co-fcc supercell

- vregime.in enables ReaxFF to determine the energy effects related to periodic cell distortion




```
#Volume regimes
#start #V type1 change/it rescale type 2  change/it  rescale
0000    2  alfa   0.050000   y     beta    -0.05       y
0100    2  beta  0.050000   y     alfa    -0.05       y
0200    2  a       0.010000   y     b       -0.010      y
0300    2  a      -0.010000   y     b        0.010      y
0400    4  a      -0.010000   y     alfa     0.050      y    b  0.01    y  beta  0.05    y
```

Electric field manipulation



Distance, angle and torsion restraints

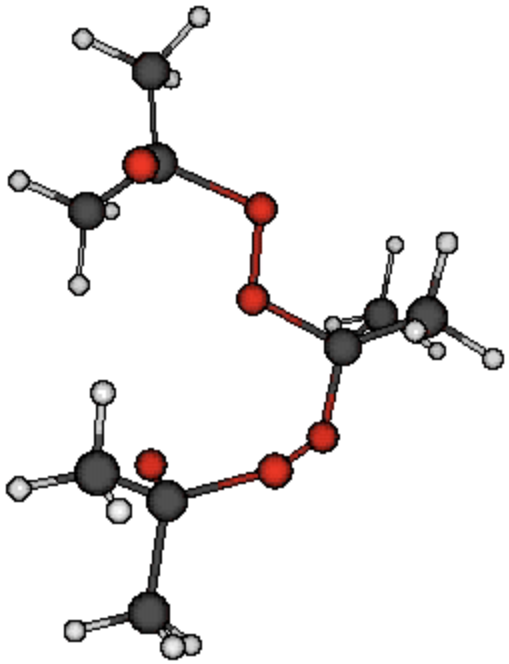
geo-file with permanent, non-sliding bond restraint

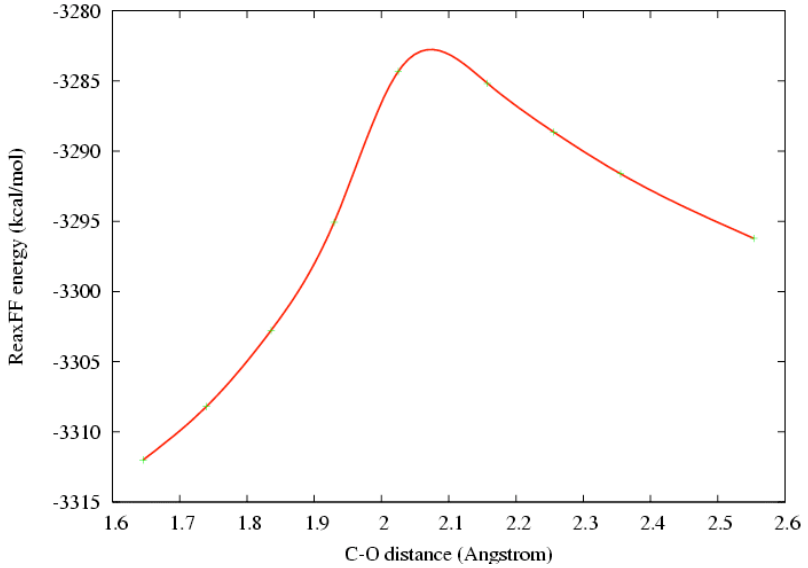
```
BIOGRF 200
DESCRP TATP_TS2_1
REMARK
#                    At1 At2   R12    Force1  Force2
BOND RESTRAINT    9  10  1.6500 2500.00  1.0000
FORMAT ATOM   (a6,1x,i5,1x,a5,1x,a3,1x,a1,1x,a5,3f10.5,1x,a5,i3,i2,1x,f8.5)
HETATM     1 C            41.60848  39.67456  37.39565    C   1 1  0.00000
HETATM     2 C            41.46109  40.16349  38.86493    C   1 1  0.00000
HETATM     3 C            42.87453  39.74506  39.36694    C   1 1  0.00000
HETATM     4 O            40.31900  39.45925  39.67087    O   1 1  0.00000
HETATM     5 O            40.37896  38.11569  39.58336    O   1 1  0.00000
HETATM     6 C            39.10337  37.50562  40.43856    C   1 1  0.00000
HETATM     7 C            38.78025  36.03359  39.92279    C   1 1  0.00000
HETATM     8 O            41.14857  41.52361  38.95930    O   1 1  0.00000
.....
.....
END
```

Distance restraint information (atoms, R_{ij}, p_{res1}, p_{res2})

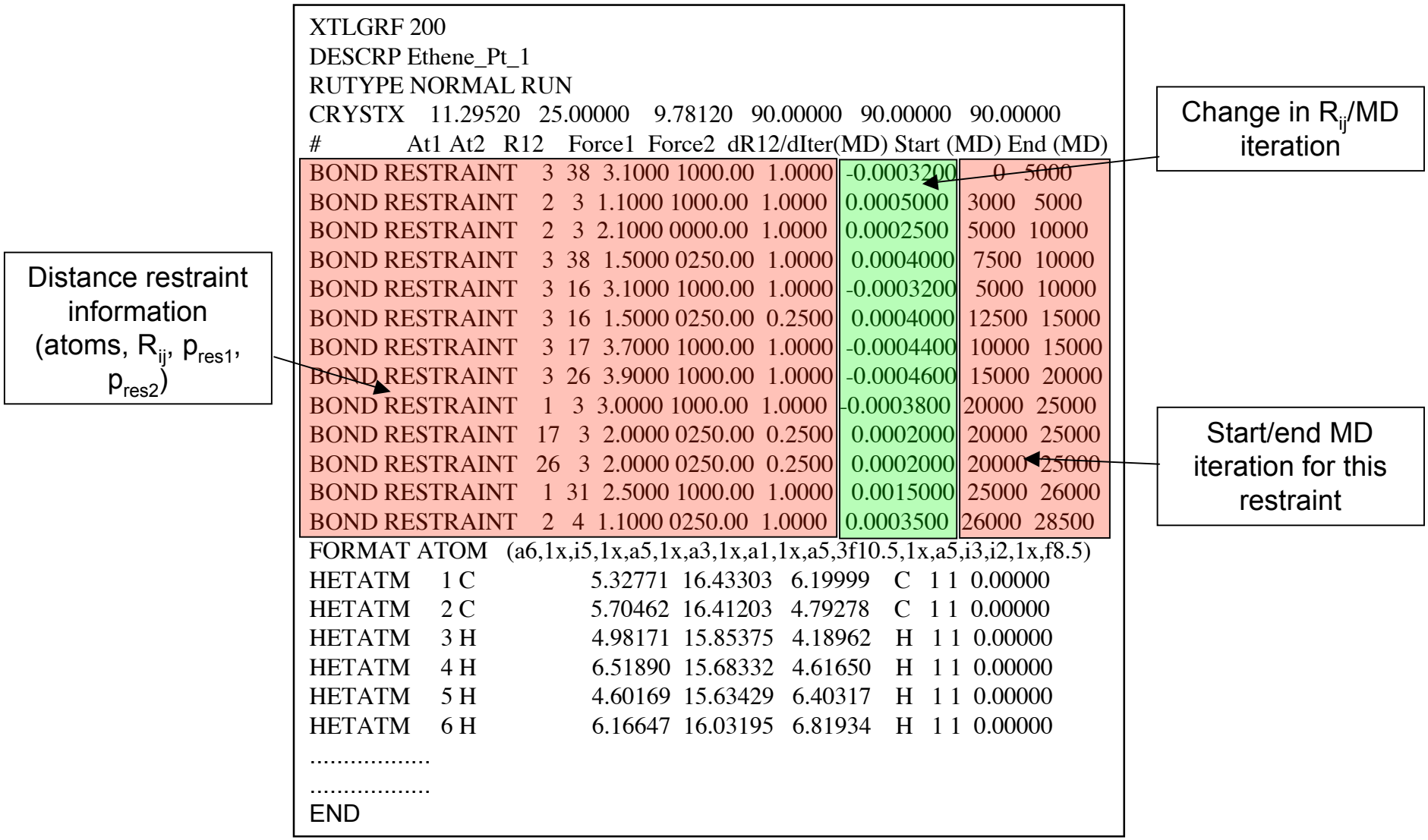
$$E_{res} = p_{res1} \cdot \left\{ 1 - \exp\left[p_{res2} \cdot \left(r_{ij} - R_{ij}^{res} \right)^2 \right] \right\}$$

- Similar format for angle and torsion restraint
- ReaxFF can also define a restraint between centres-of-mass for groups of atoms



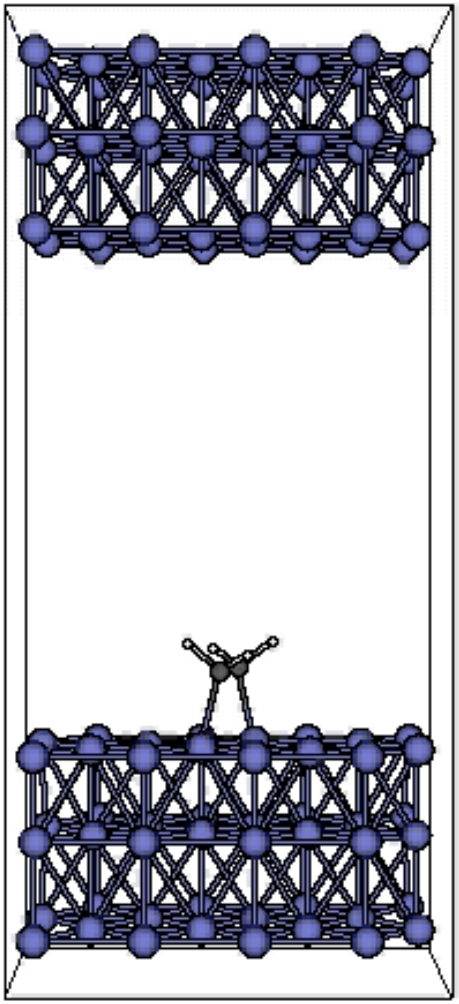

-3280
-3285
-3290
-3295
-3300
-3305
-3310
-3315
ReaxFF energy (kcal/mol)
1.6
1.7
1.8
1.9
2
2.1
2.2
2.3
2.4
2.5
2.6
C-O distance (Angstrom)

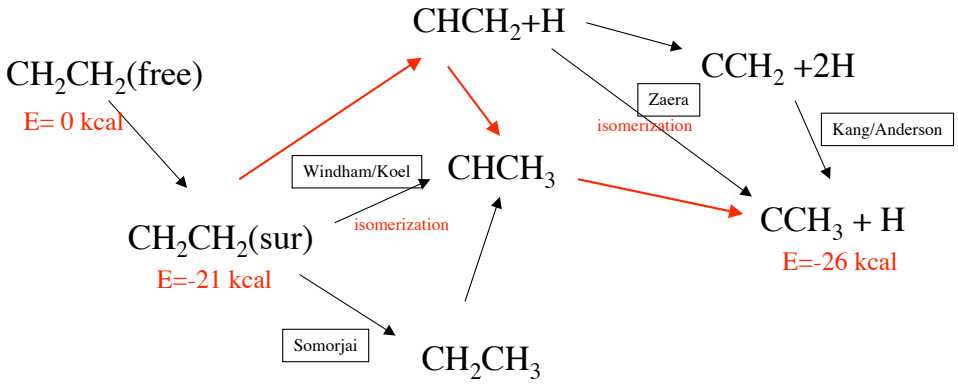
geo-file with programmed sliding restraints

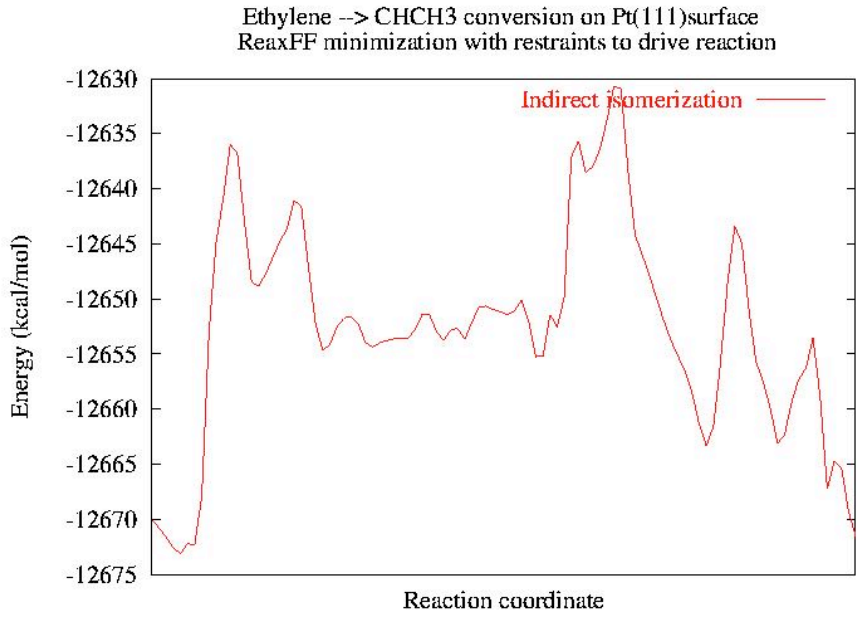


- Only available for MD-simulation

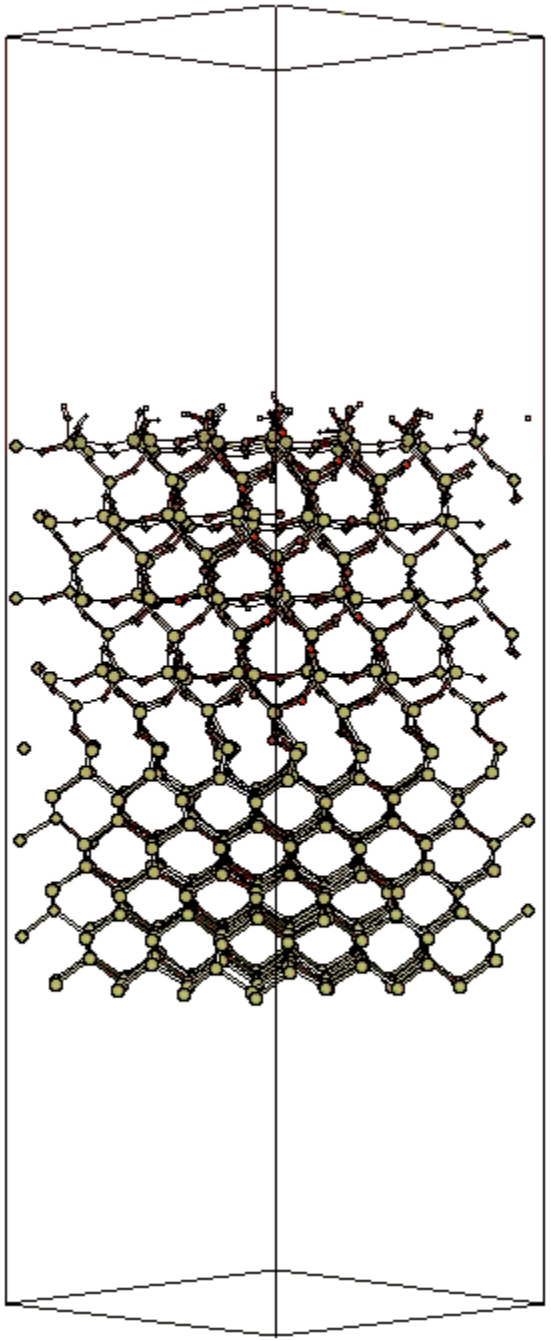
ReaxFF MD-simulation using sliding bond restraints to drive reactions

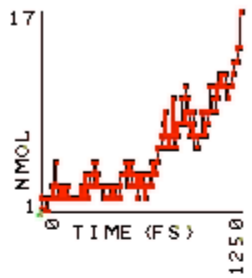


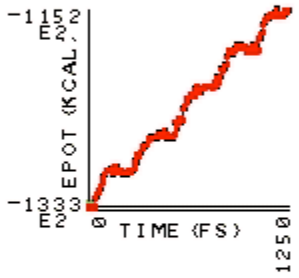


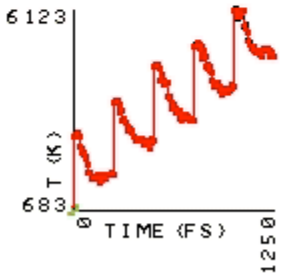


Adding molecules during an MD-simulation










```
BIOGRF 200
DESCRP Si_atom
FREQADD   100
VELADD  2
STARTX -9000.0
STARTY    60.0
STARTZ -9000.0
ADDIST 3.0
NATTEMPT 050
TADDMOL 250.0
FORMAT ATOM   (a6,1x,i5,1x,a5,1x,a3,1x,a1,1x,a5,3f10.5,1x,a5,i3,i2,1x,f8.5)
HETATM     1 Si              0.00000   0.00000   0.00000 Si      1 3  0.00000
END
```

addmol.bgf

```
Atom velocities (Angstrom/s):
 0.676920600871422E+13  -0.400000000000001E+15   0.685204179579294E+03
```

addmol.vel

- Copied moldyn.vel from earlier 600K-equilibration run to vels
- Other input files : exe, control, geo, ffield

Force field development for Si/SiO systems

$$E_{system} = E_{bond} + E_{over} + E_{val} + \cancel{E_{tors}} + E_{vdWaals} + E_{Coulomb}$$

Covalent materials

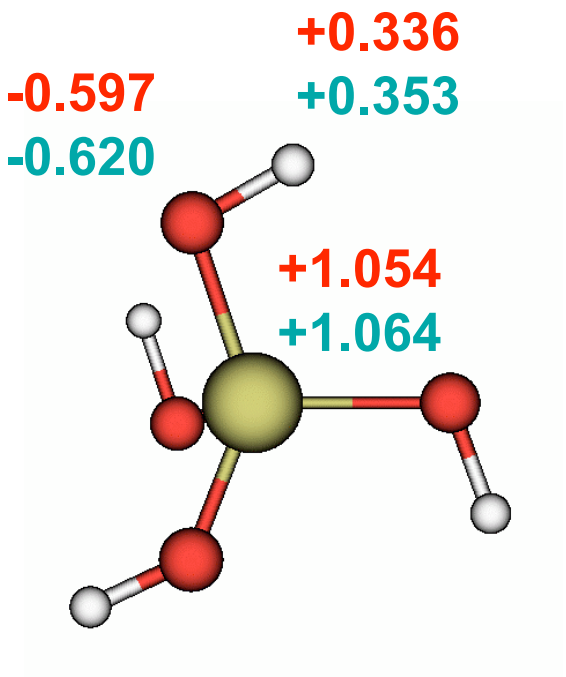
- E_{bond}: bond energy; attractive term, directly derived from bond orders
- E_{over}: Overcoordination energy: penalty for overcoordinating atoms
- E_{val}: Angle strain; equilibrium angle depends on bond order central atom
- E_{tors}: Torsion energy: bond-order dependent V_2-term
- $E_{vdWaals}$: van der Waals: calculated between every atom
- $E_{Coulomb}$: Coulomb interaction: calculated between every atom

- Concept: build a QM-based database (training set) that describes reactive and non-reactive aspects of the material and optimize ReaxFF to reproduce these QM-data.
- Bigger (more extensive) training sets yield more transferable force fields (but longer development time!)
- Things to include in training sets: charges, bond dissociation, angle bending, under/overcoordination, key reactions with transition states, equations of state

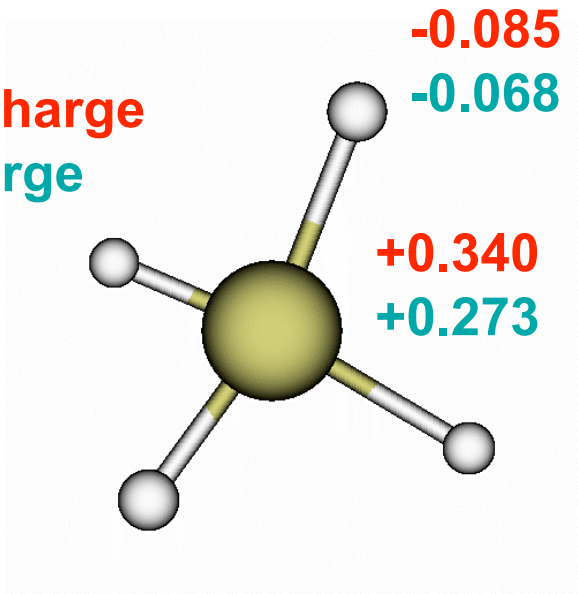
Adri van Duin, Alejandro Strachan, Shannon Stewman, Qingsong Zhang, Xin Xu and Bill Goddard, Journal of Physical Chemistry-A 2003

Charges

- Fit atom electronegativities and hardnesses to QM-based charge distributions

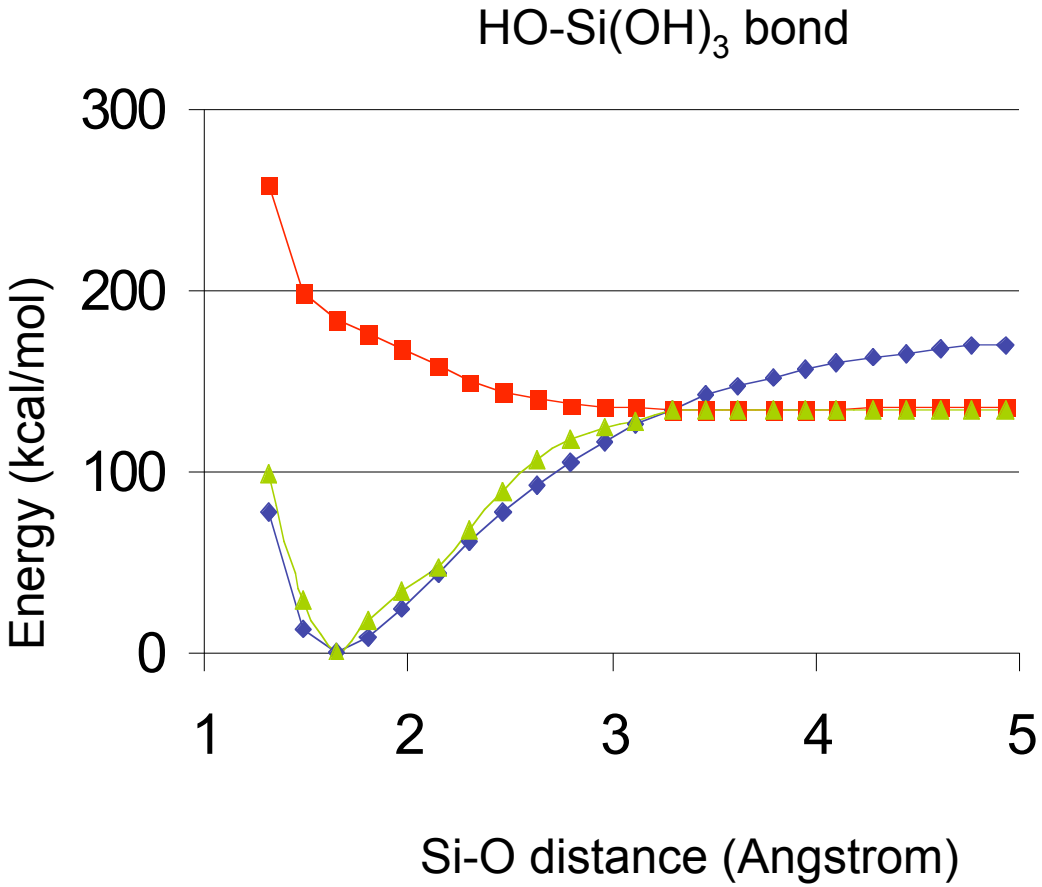


QM/Mulliken charge
ReaxFF charge



$$E_{system} = E_{bond} + E_{over} + E_{val} + E_{vdWaals} + E_{Coulomb}$$

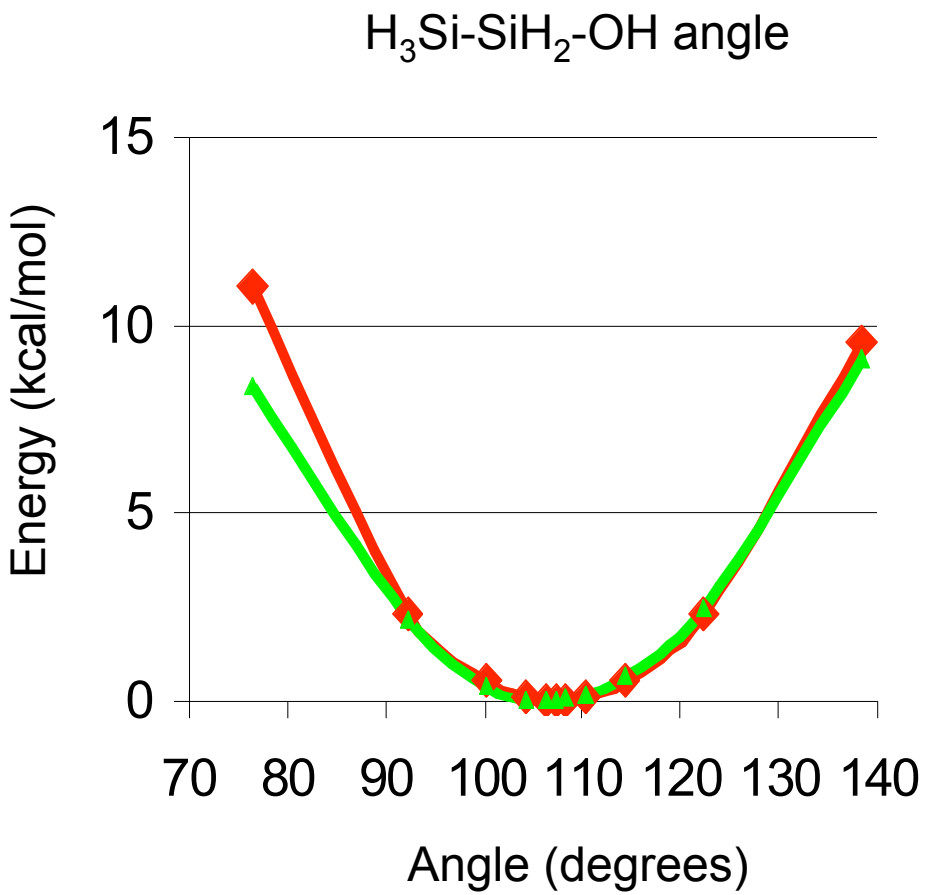
Bond energy



Other SiOH bonds:
- Si-Si
- Si=Si
- Si=O
- Si-H
- O-O
- O=O
- O-H

$$E_{system} = E_{bond} + E_{over} + E_{val} + E_{vdWaals} + E_{Coulomb}$$

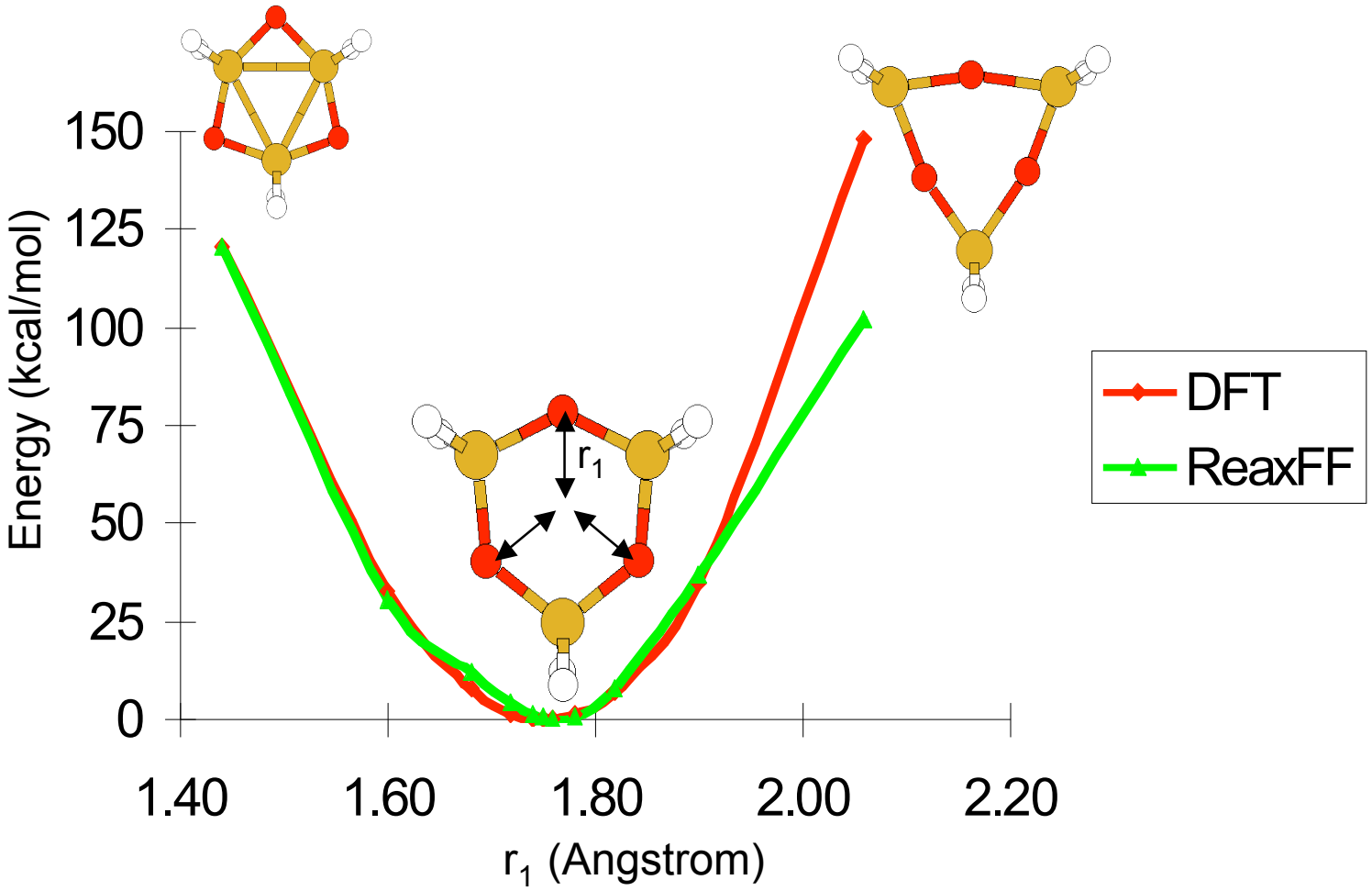
Valence angle bending
1. Individual valence angles



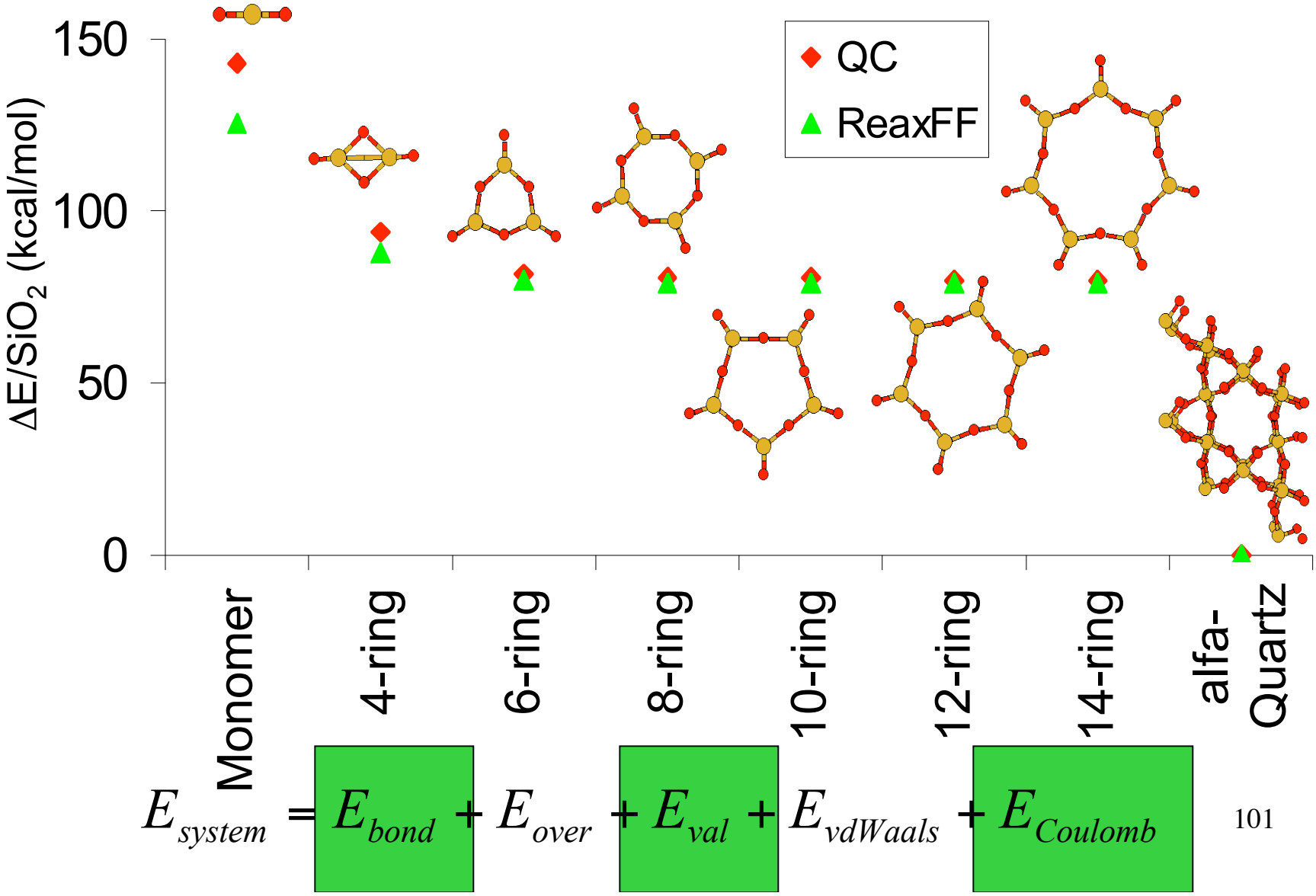
Other SiOH angles:

- Si-Si-Si
- Si-O-Si
- Si-Si-H
- Si-O-H
- O-Si-H
- Si-Si-H
- H-Si-H
- H-O-H
- O-O-O
- Si-O-O
- O-O-H

Valence angle bending
2. Ring deformation



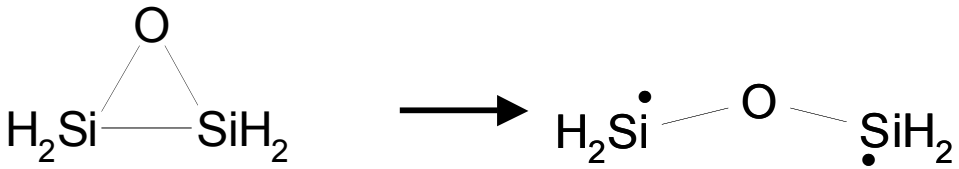
Valence angle bending
3. Ring size/ring strain



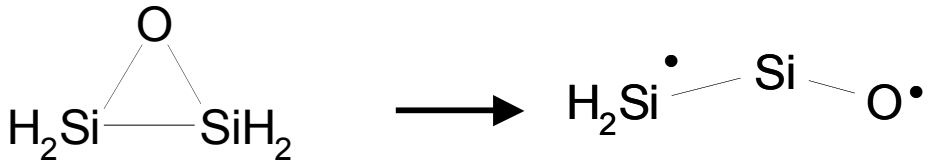
$$E_{system} = E_{bond} + E_{over} + E_{val} + E_{vdWaals} + E_{Coulomb}$$

Over/undercoordination

		ΔE (DFT)	ΔE(ReaxFF)
$Si(OH)_4$ + HO-OH	→ $Si(OH)_6$	+60.9 kcal/mol	+48.2 kcal/mol
H_3Si-O-SiH_3 + H_3Si-SiH_3	→ $O(SiH_3)_4$	+102.5 kcal/mol	+87.4 kcal/mol



+28.4 kcal/mol +35.1 kcal/mol

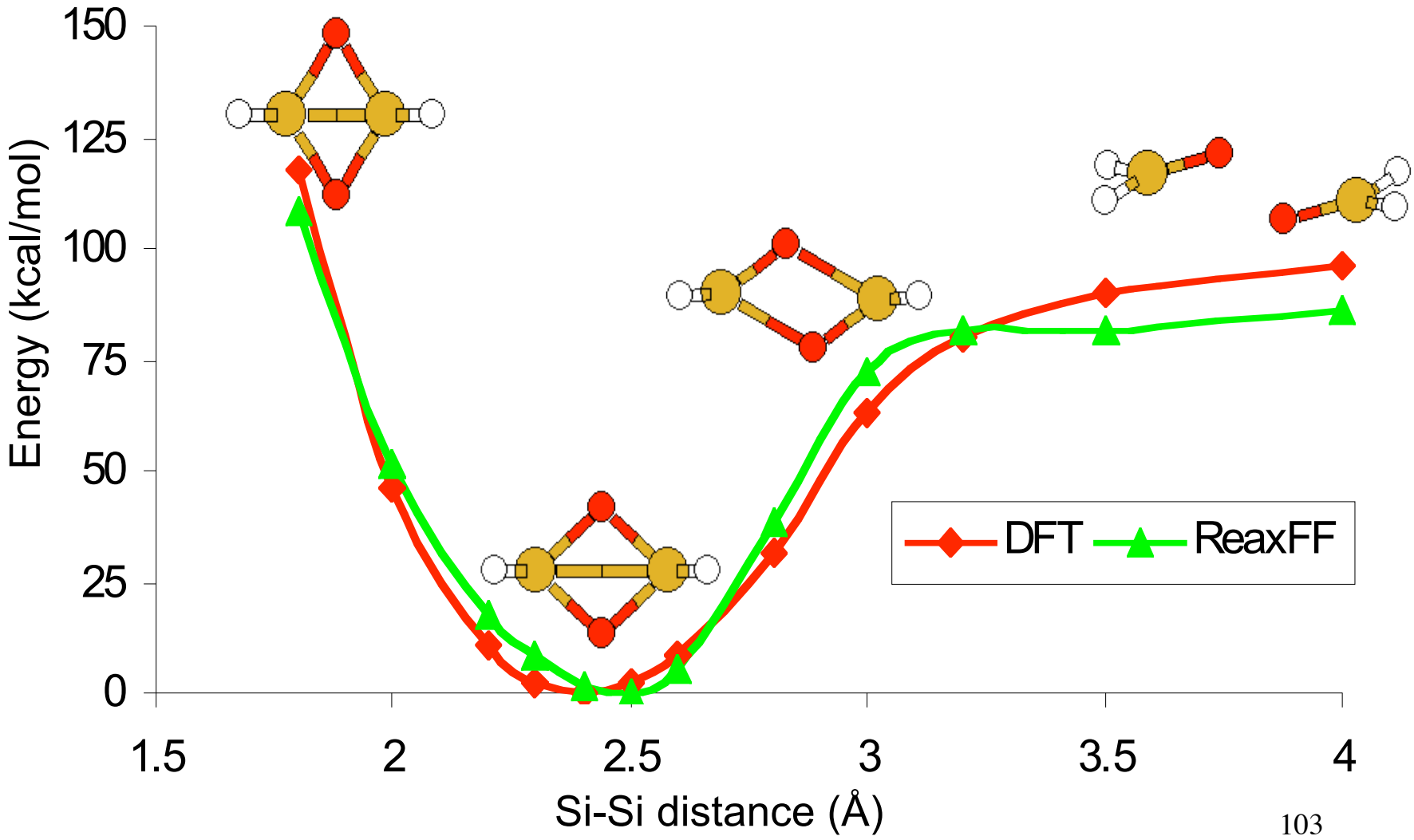


+67.8 kcal/mol +75.5 kcal/mol

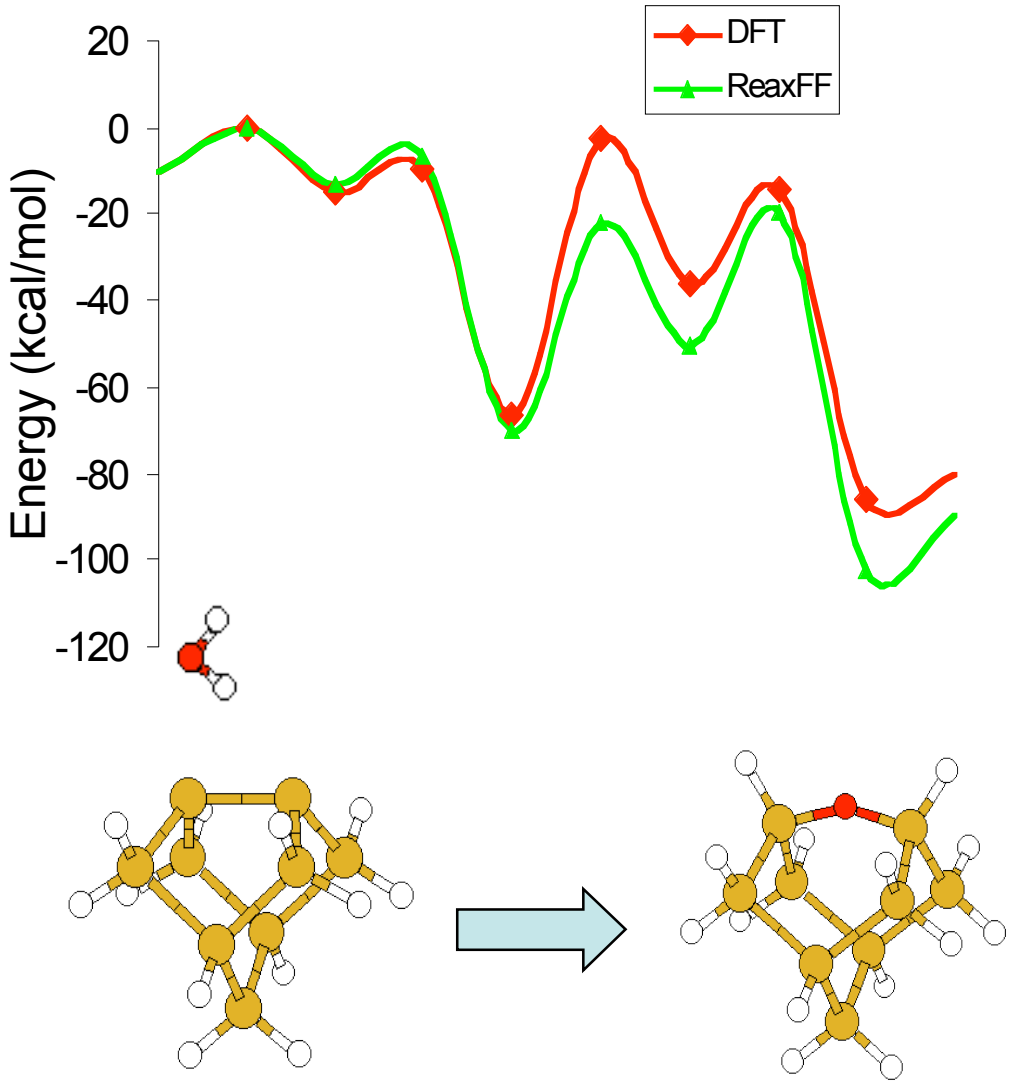
$$E_{system} = E_{bond} + E_{over} + E_{val} + E_{vdWaals} + E_{Coulomb}$$

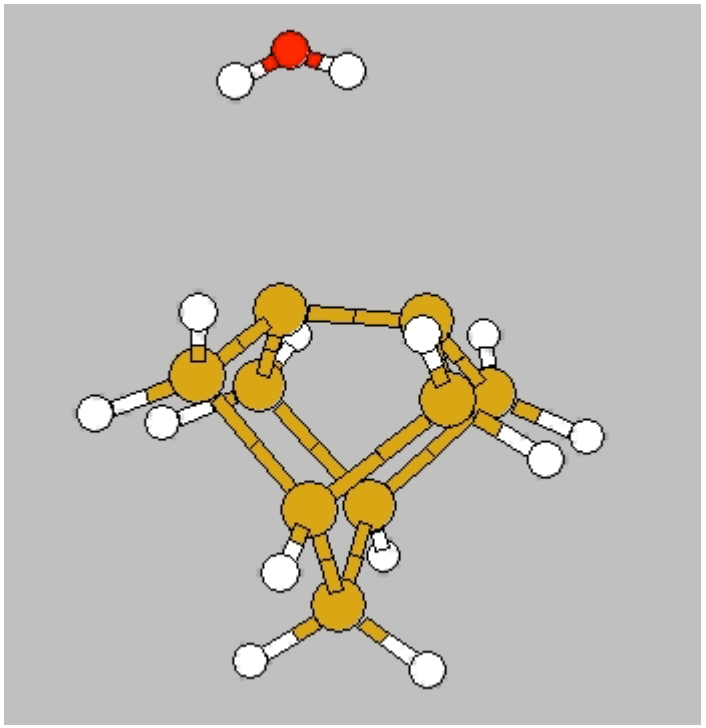
Reactions

1. $H_2Si=O + H_2Si=O \rightarrow$ 4-ring



Reactions
2. H_2O- incorporation in a Si-cluster

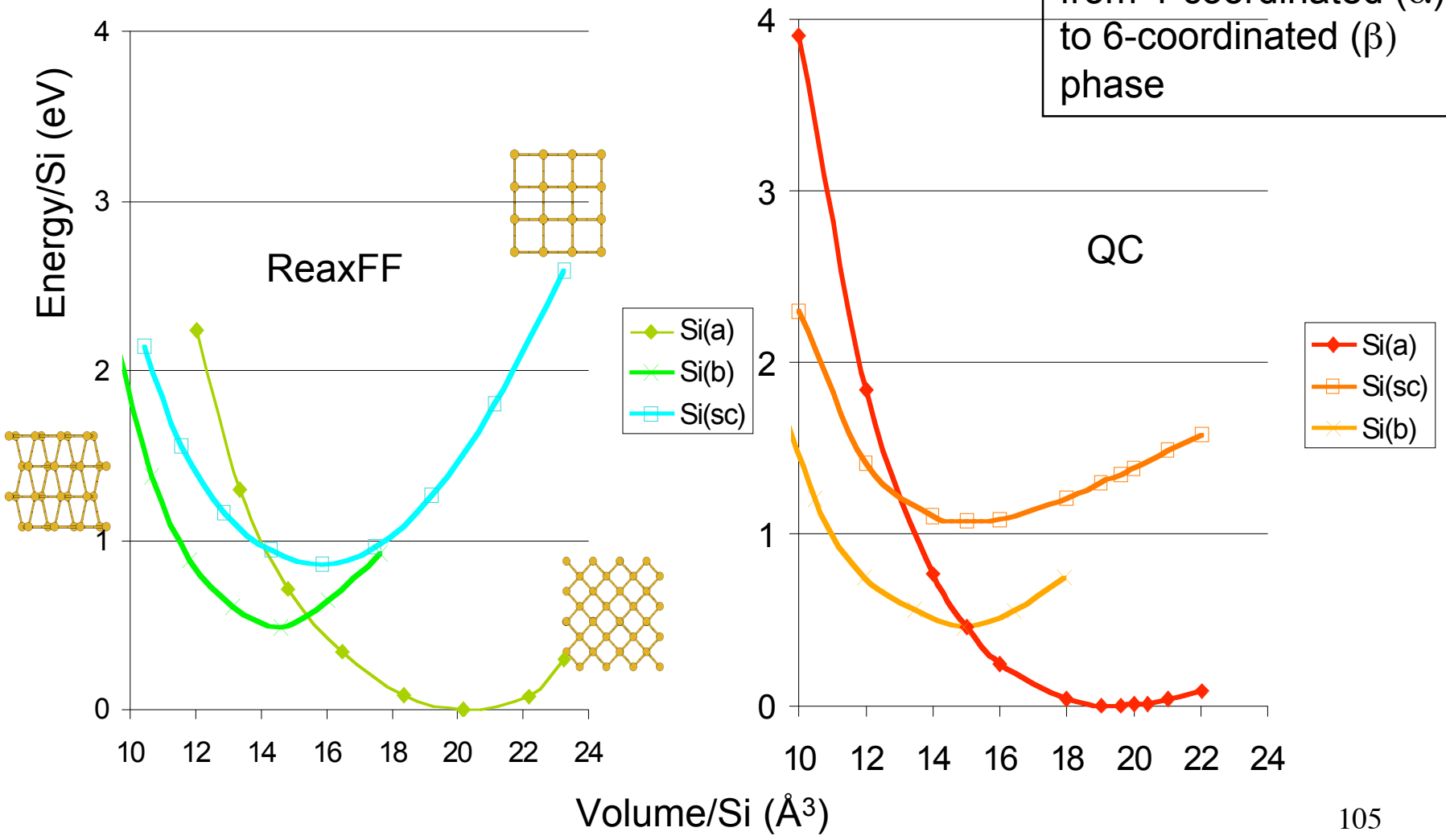




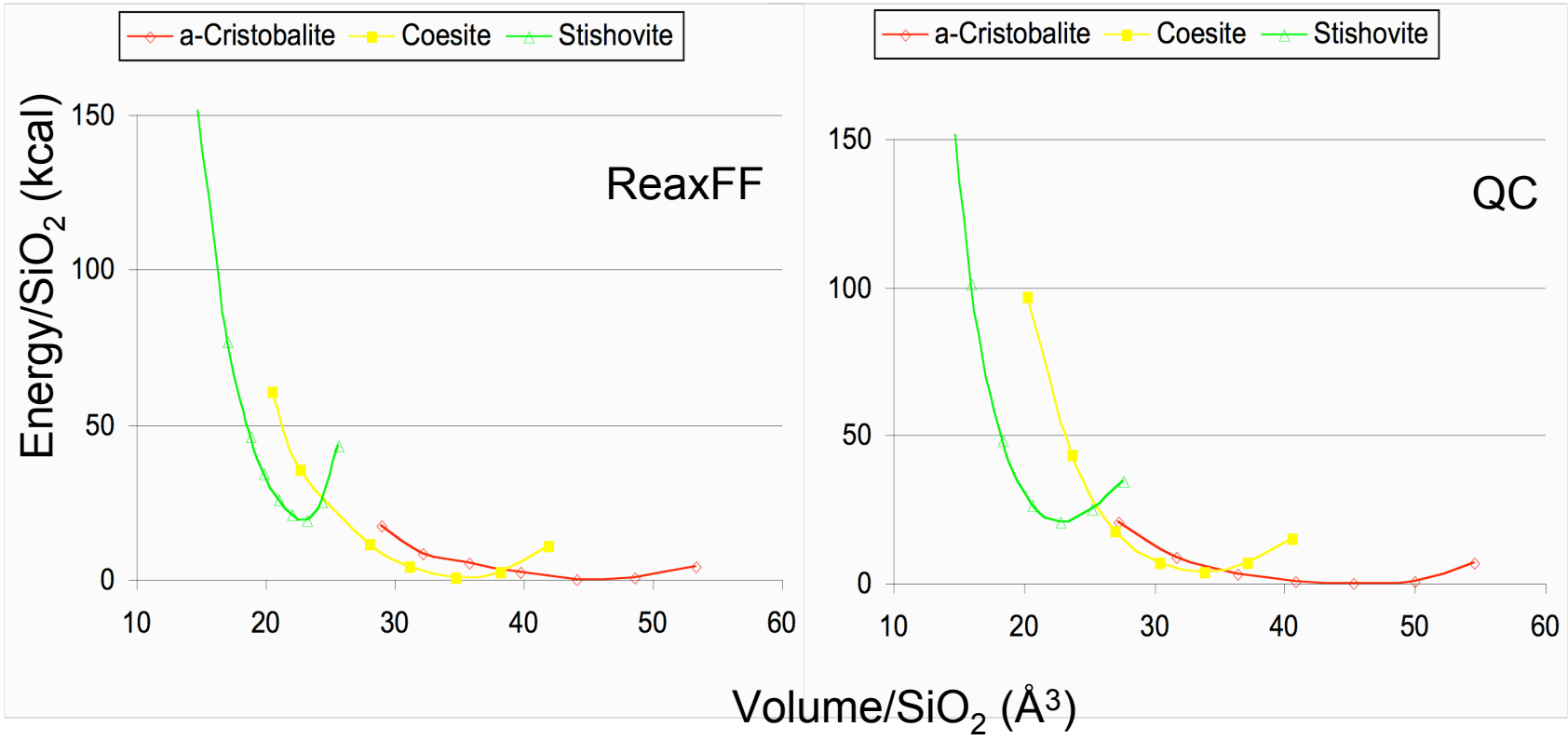
- Reactive force field can be used to simulate the entire reaction pathway

Equations of state crystals
1. All-Si crystals

- Force field recognizes high-pressure transition from 4-coordinated (α) to 6-coordinated (β) phase



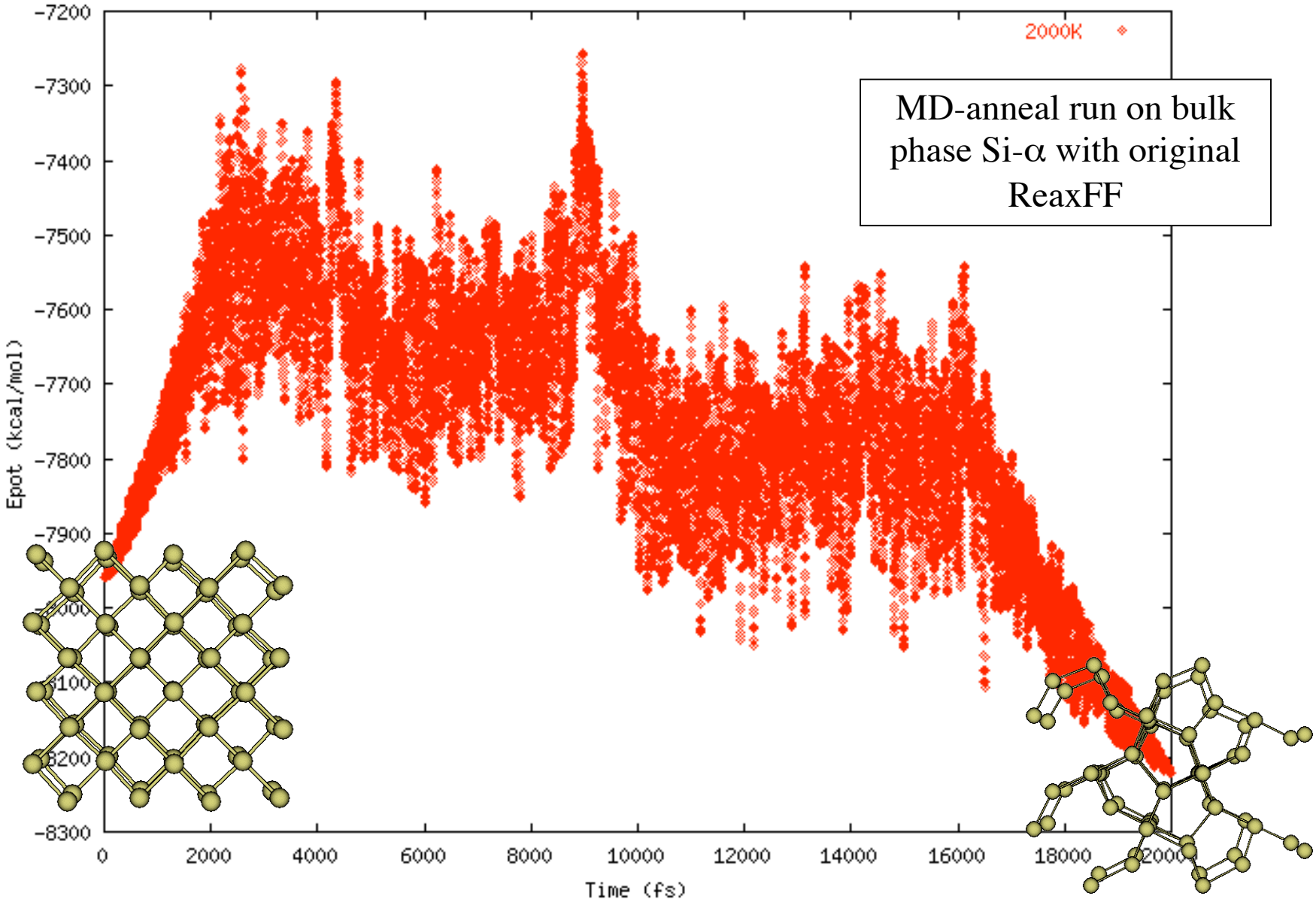
Compression/expansion crystals
2. Silicon oxide crystals



- ReaxFF reproduces the QC-data for both the clusters as well as the condensed phases.

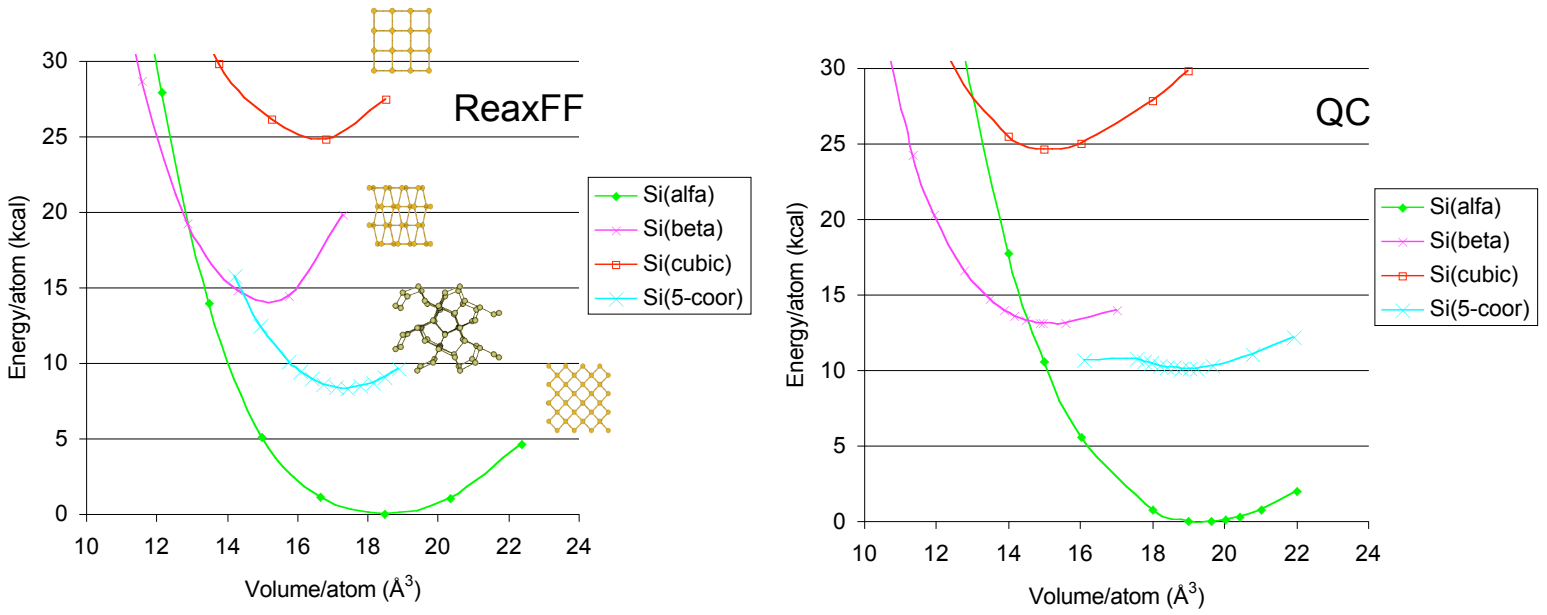
$$E_{system} = E_{bond} + E_{over} + E_{val} + E_{vdWaals} + E_{Coulomb}$$

Correcting a ‘finished’ ReaxFF force field



- Original ReaxFF overstabilizes 5-coordination for silicon bulk phase

Re-optimize ReaxFF with equation of state for 5-coordinate Si-phase



- Re-optimized ReaxFF gets proper stability for 5-coordinate Si-phase
- 5-coordinate phase is more stable than 6-coordinate Si(β) !
- 5-coordinate Si might be important in amorphous Si

MD-anneal run on bulk phase Si-α with ReaxFF