

# Using the ReaxFF program

Adri van Duin

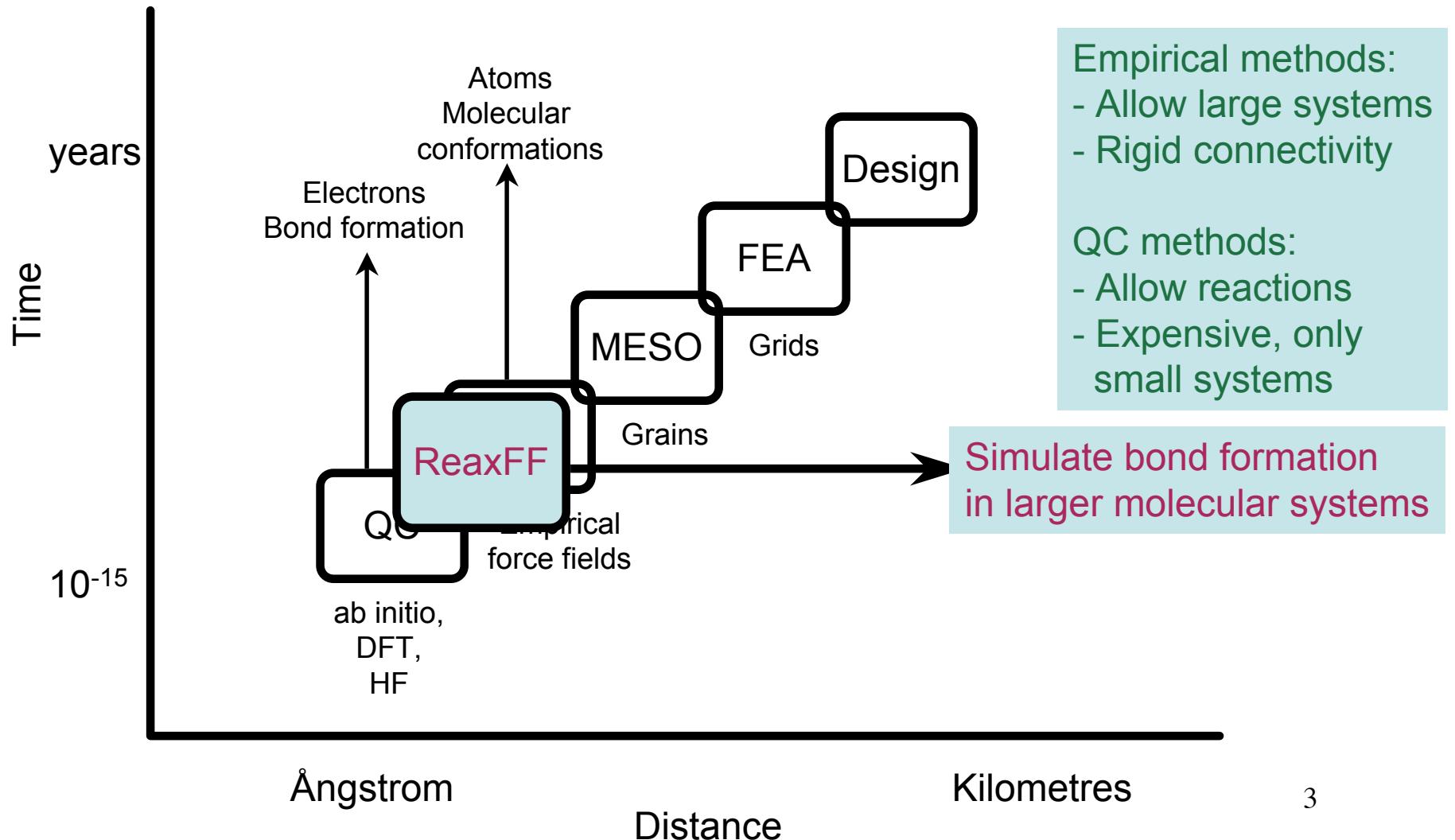
Training session at NASA AMES

August 2006

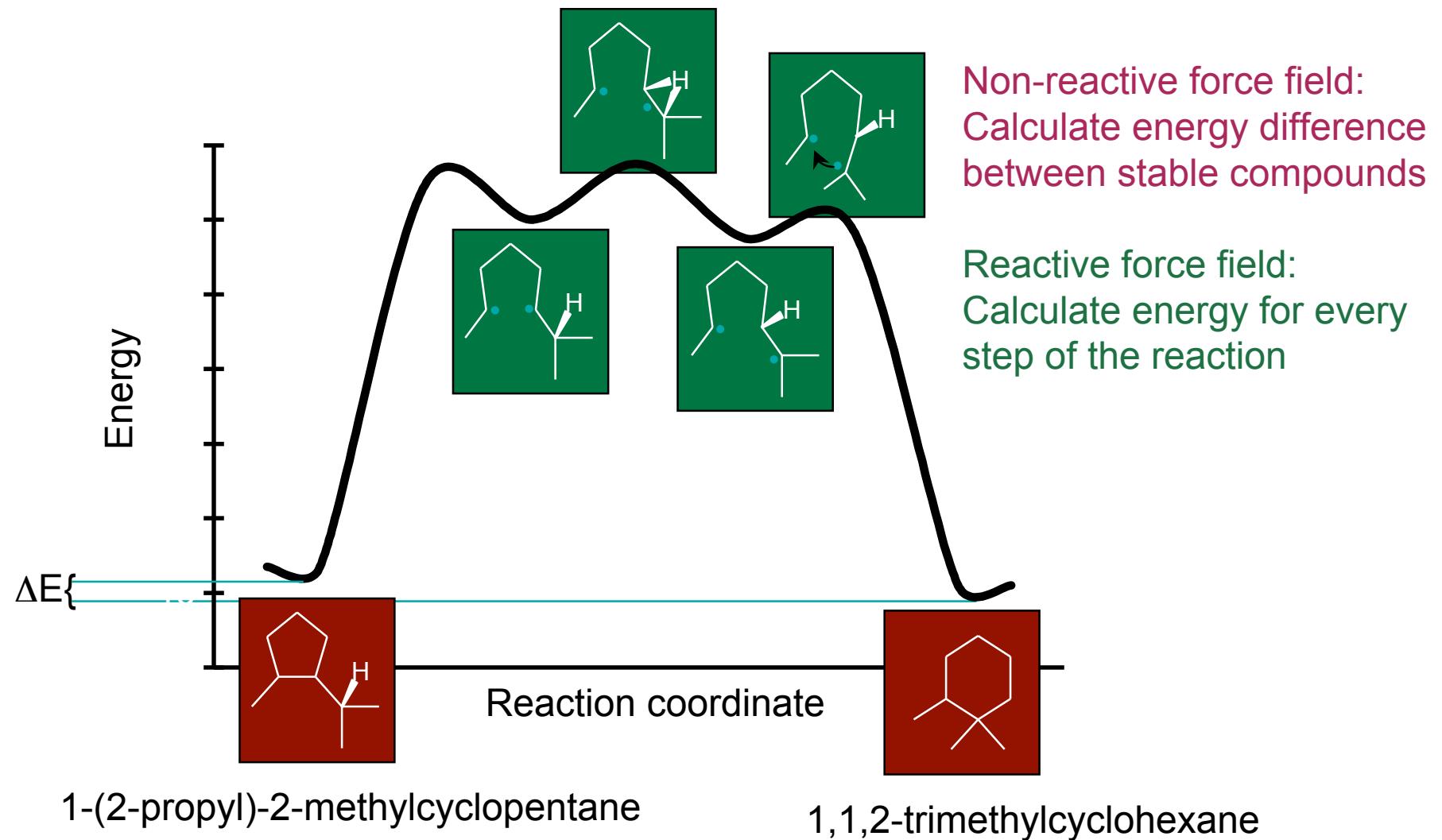
# Contents

- ReaxFF background and rules (expanded)
- ReaxFF program structure
- Overview ReaxFF in- and output files
  - General
  - MD-simulations
  - Energy minimization
- Examples:
  - Si particle oxidation
  - Si-surface impact on SiO<sub>2</sub>/Si
  - Force field development
- Additional ReaxFF features
  - Multiple thermostats
  - Cell volume manipulation
  - Electric field
  - Bond, angle and torsion restraints
  - Introduction of new molecules during MD-simulation

# ReaxFF: background and rules



# Reactive vs. non-reactive force fields



## ReaxFF system energy description

$$E_{system} = \underbrace{E_{bond} + E_{vdWaals} + E_{Coulomb}}_{\text{2-body}} + E_{val} + E_{tors} + \underbrace{E_{over} + E_{under}}_{\text{multibody}}$$

3-body      4-body

## Key features

- To get a smooth transition from nonbonded to single, double and triple bonded systems ReaxFF employs a bond length/bond order relationship. Bond orders are updated every iteration.
- Nonbonded interactions (van der Waals, Coulomb) are calculated between **every** atom pair, irrespective of connectivity. Excessive close-range nonbonded interactions are avoided by shielding.
- All connectivity-dependent interactions (i.e. valence and torsion angles) are made bond-order dependent, ensuring that their energy contributions disappear upon bond dissociation.
- ReaxFF uses a geometry-dependent charge calculation scheme that accounts for polarization effects.

# Connectivity: differences in program structure

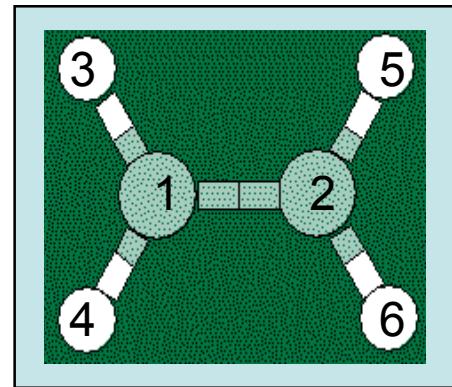
## Non-reactive force field

1:  $x_1 \ y_1 \ z_1$   
2:  $x_2 \ y_2 \ z_2$   
3:  $x_3 \ y_3 \ z_3$   
4:  $x_4 \ y_4 \ z_4$   
5:  $x_5 \ y_5 \ z_5$   
6:  $x_6 \ y_6 \ z_6$

Atom positions

1: 2 3 4  
2: 1 5 6  
3: 1  
4: 1  
5: 2  
6: 2

Connection table



## Reactive force field

1:  $x_1 \ y_1 \ z_1$   
2:  $x_2 \ y_2 \ z_2$   
3:  $x_3 \ y_3 \ z_3$   
4:  $x_4 \ y_4 \ z_4$   
5:  $x_5 \ y_5 \ z_5$   
6:  $x_6 \ y_6 \ z_6$

Atom positions

MM or MD routine

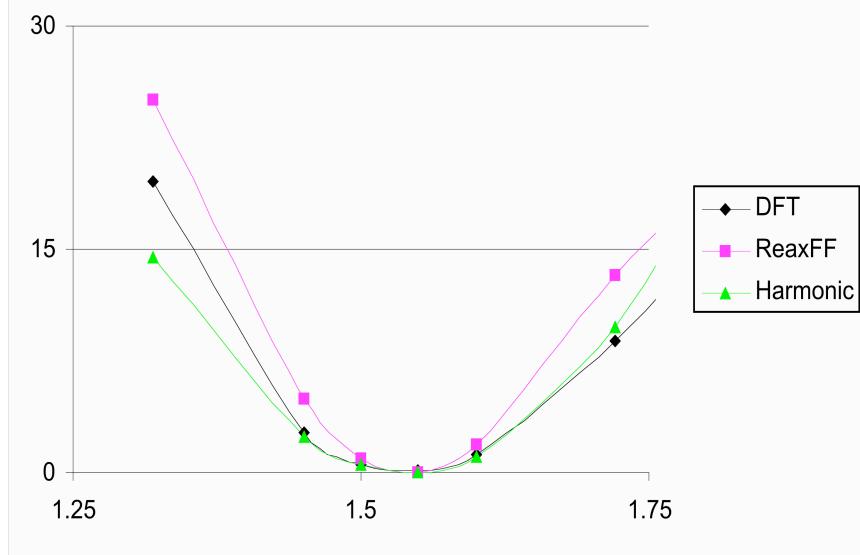
Determine connections

MM or MD routine

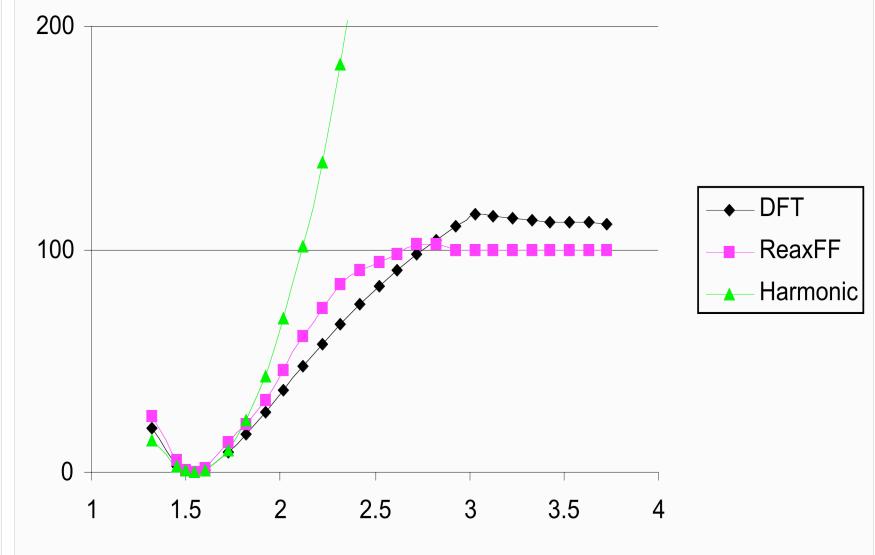
# Bonds

## C-C bond stretching in Ethane

Around the equilibrium bond length



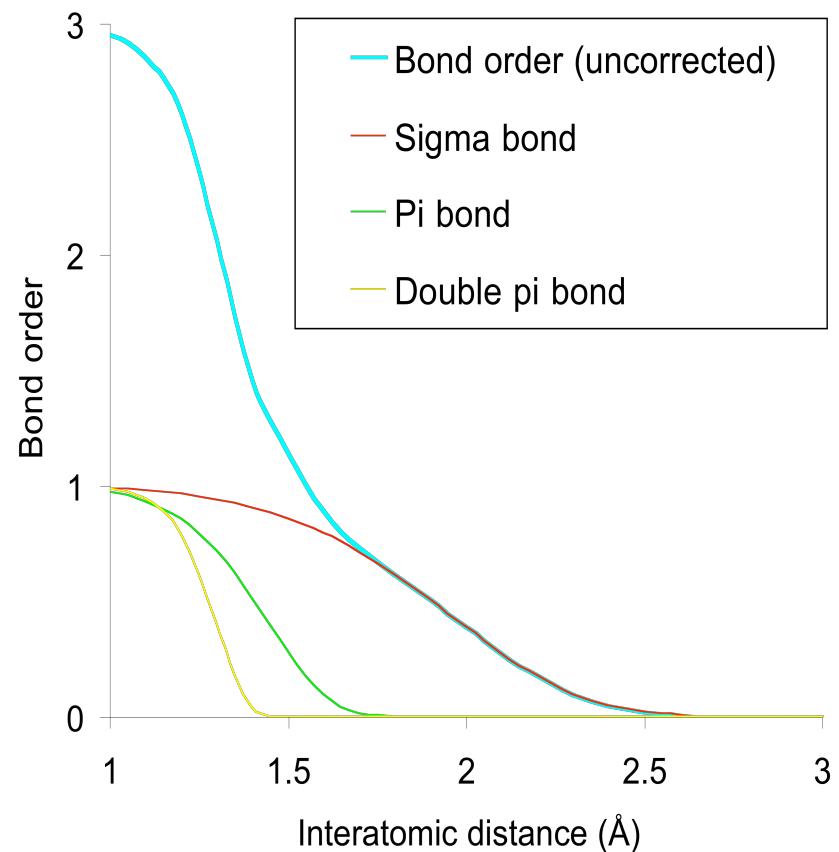
Full dissociation curve



- Although the harmonic approximation can describe the bond stretching around the equilibrium it cannot describe the bond dissociation.
- Harmonic force field needs to use multiple atom types to distinguish single, double and triple bonded carbons.

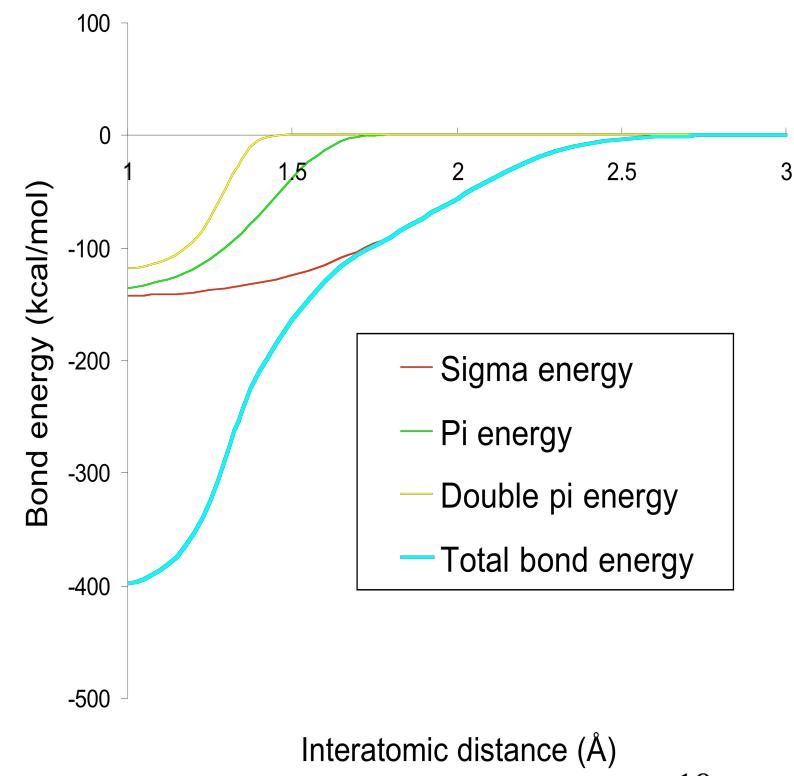
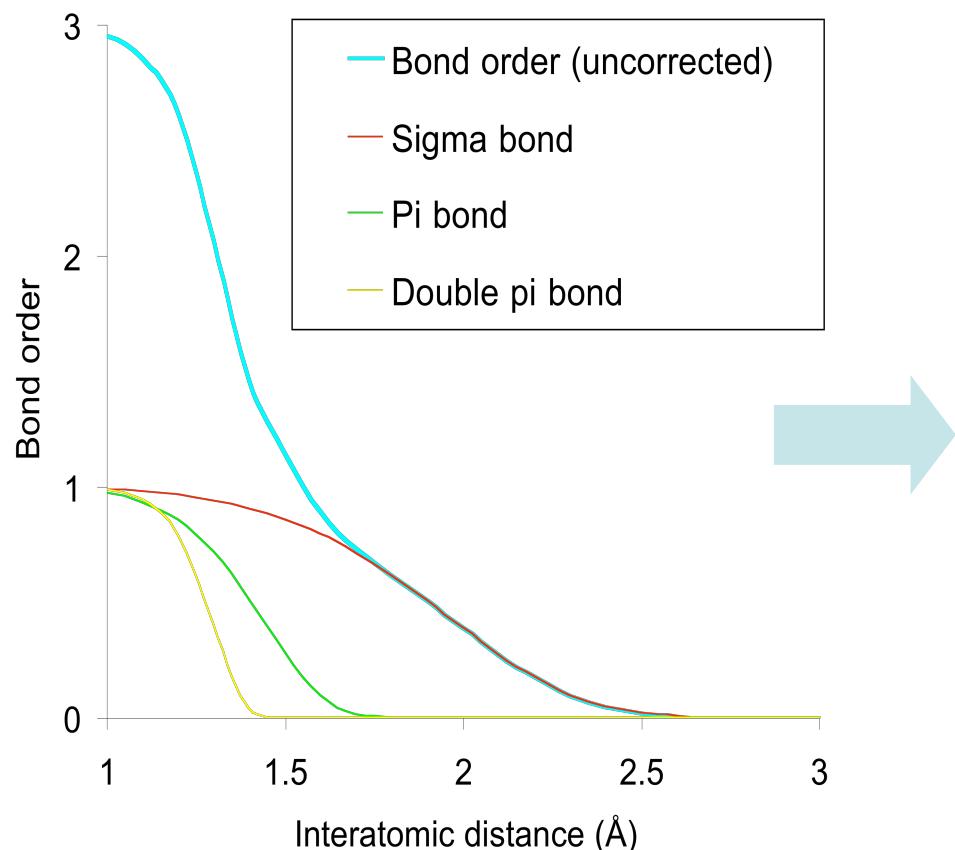
## Calculation of bond orders from interatomic distances

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



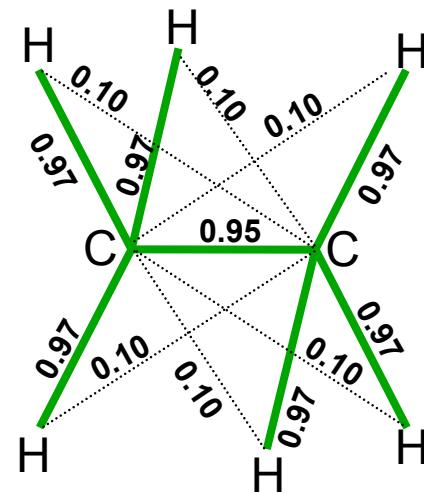
## Calculation of bond energy from bond orders

$$E_{bond} = -D_e^\sigma \cdot BO_{ij}^\sigma \cdot f(BO_{ij}^\sigma) - D_e^\pi \cdot BO_{ij}^\pi - D_e^{\pi\pi} \cdot BO_{ij}^{\pi\pi}$$



# Bond order correction

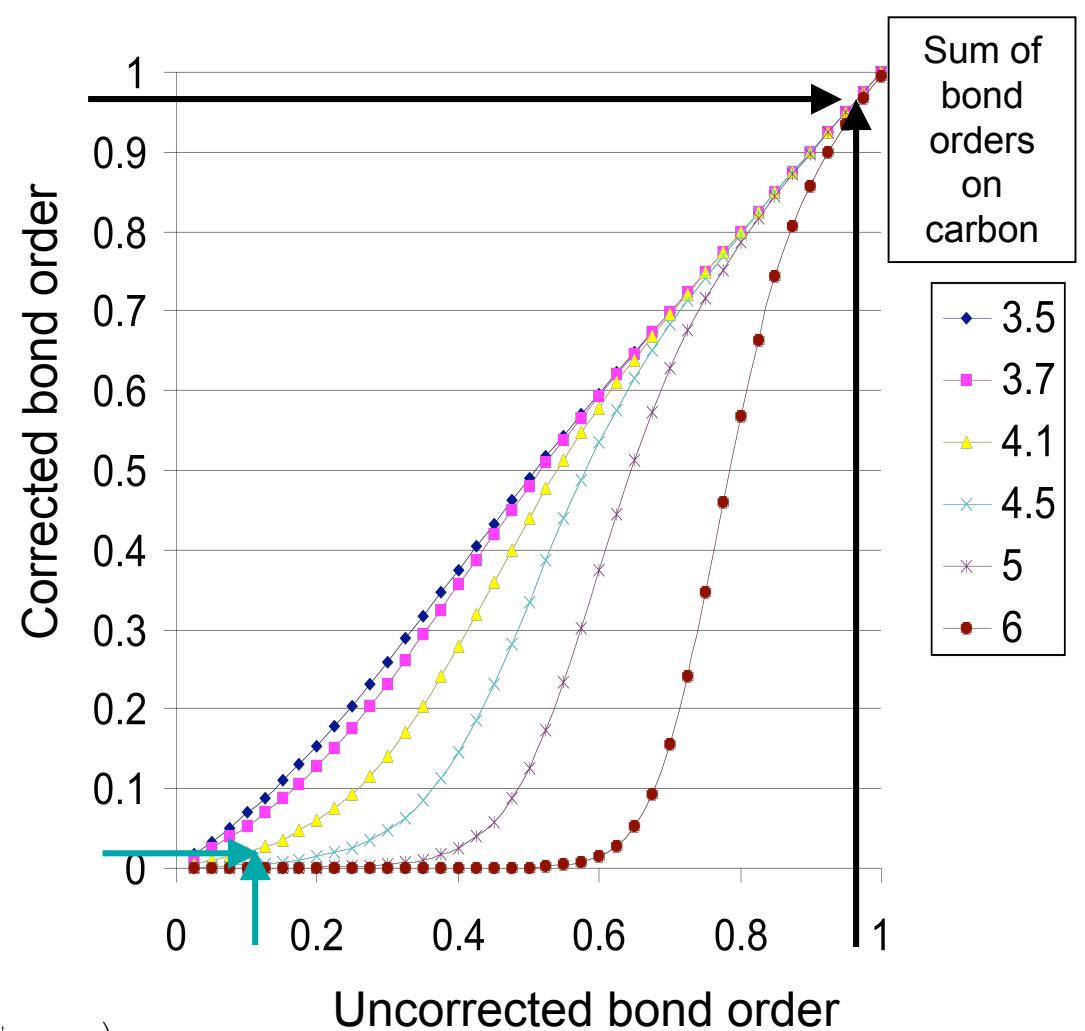
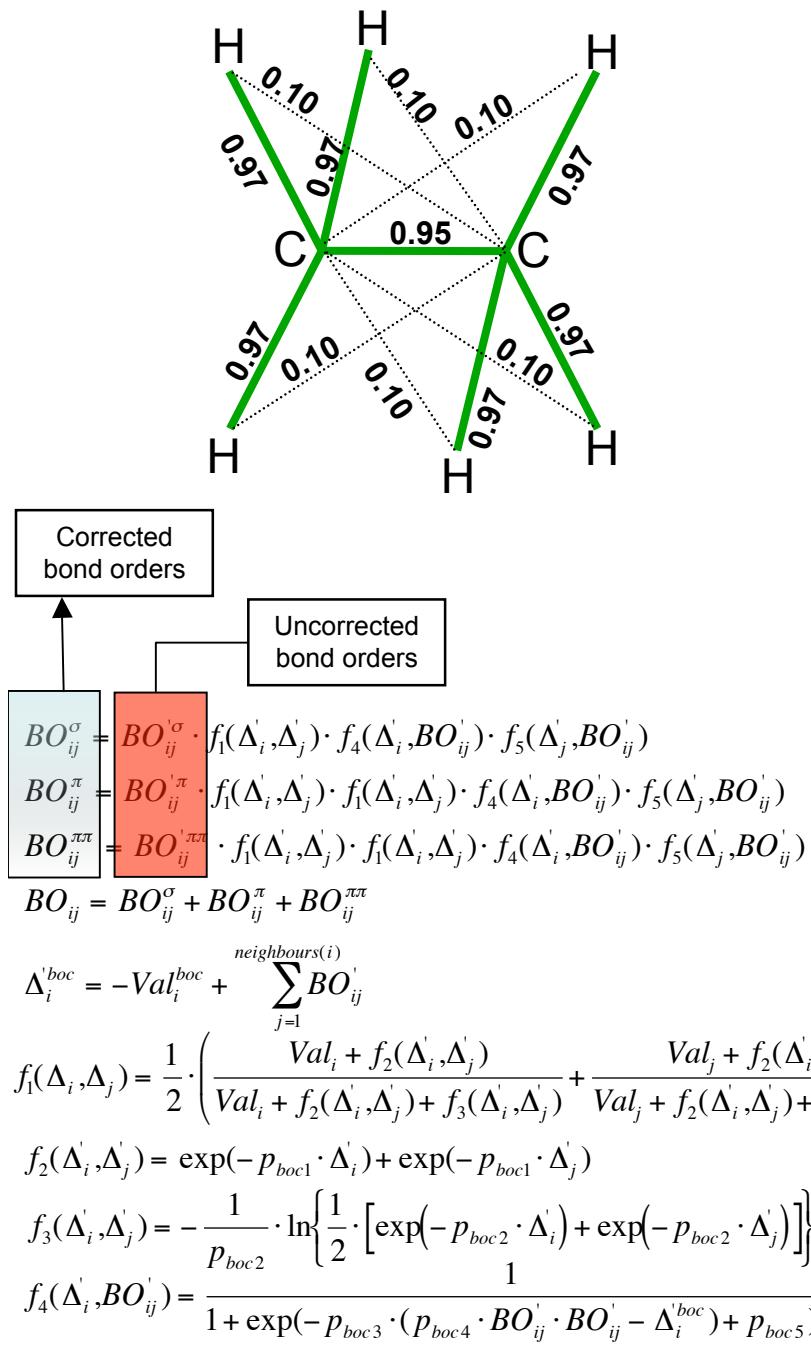
Uncorrected bond orders



$$\sum BO_C = 4.16$$

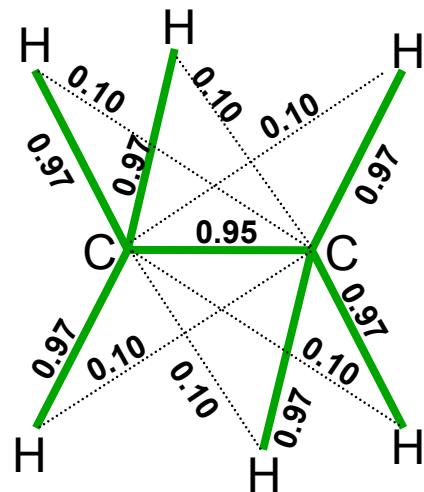
$$\sum BO_H = 1.17$$

- Unphysical; normally coordinated atoms should not have binding interactions with next-neighbours
- Puts strain on angle and overcoordination potentials



- Normally coordinated carbon will not make weak bonds, under-coordinated carbon (radical) can make weak bonds

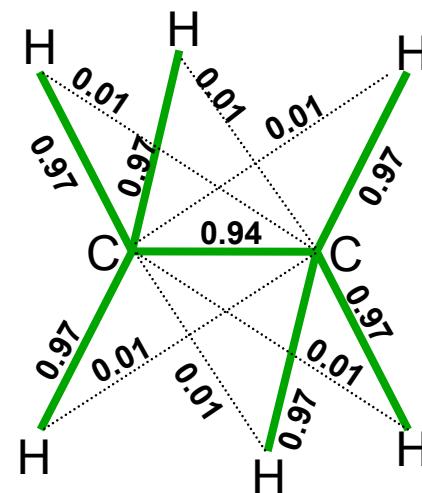
Uncorrected bond orders



$$\Sigma BO_C = 4.16$$

$$\Sigma BO_H = 1.17$$

Corrected bond orders



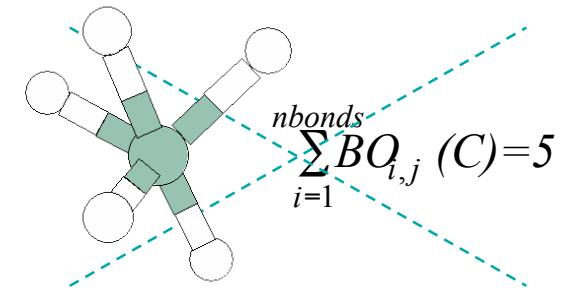
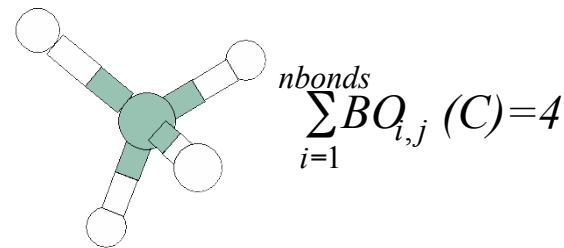
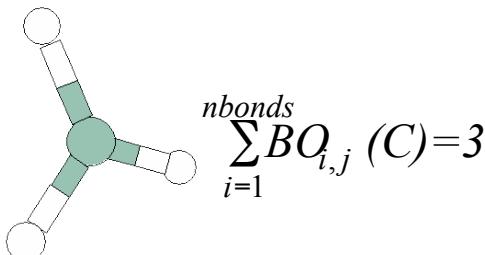
$$\Sigma BO_C = 3.88$$

$$\Sigma BO_H = 0.98$$

- 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

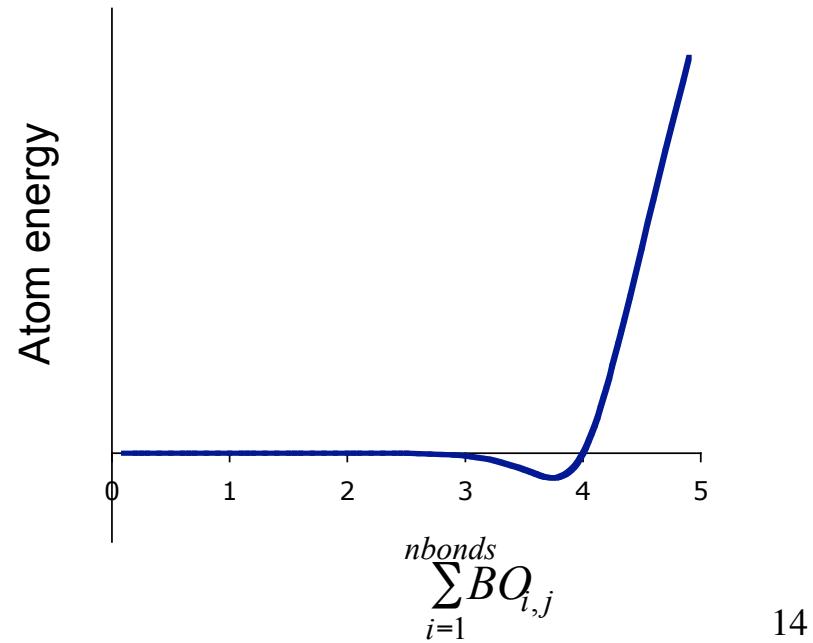
# Dealing with overcoordination in ReaxFF

Avoid unrealistically high amounts of bond orders on atoms



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

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

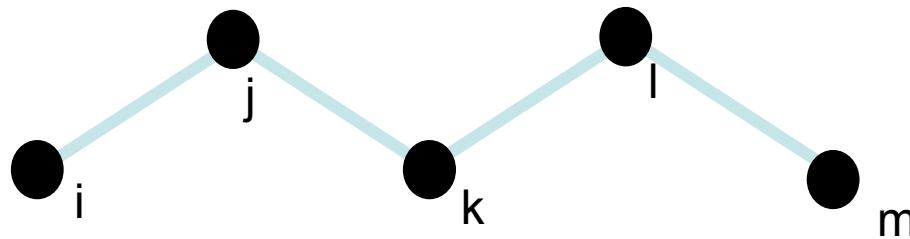


## Key features

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- ReaxFF uses a geometry-dependent charge calculation scheme that accounts for polarization effects.

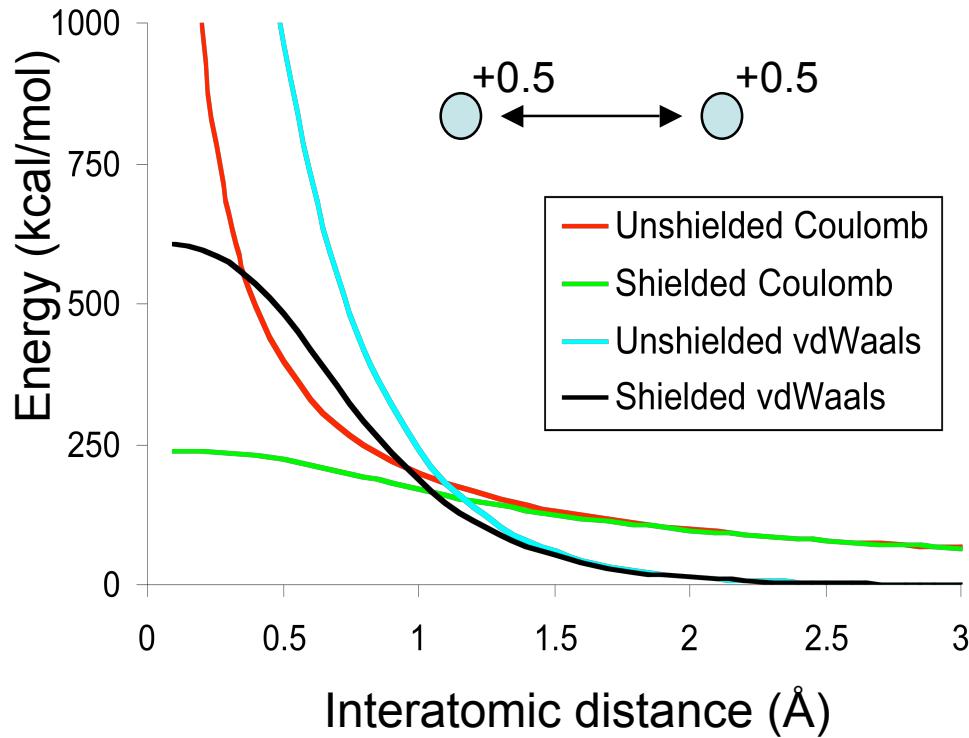
## Nonbonded interactions



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

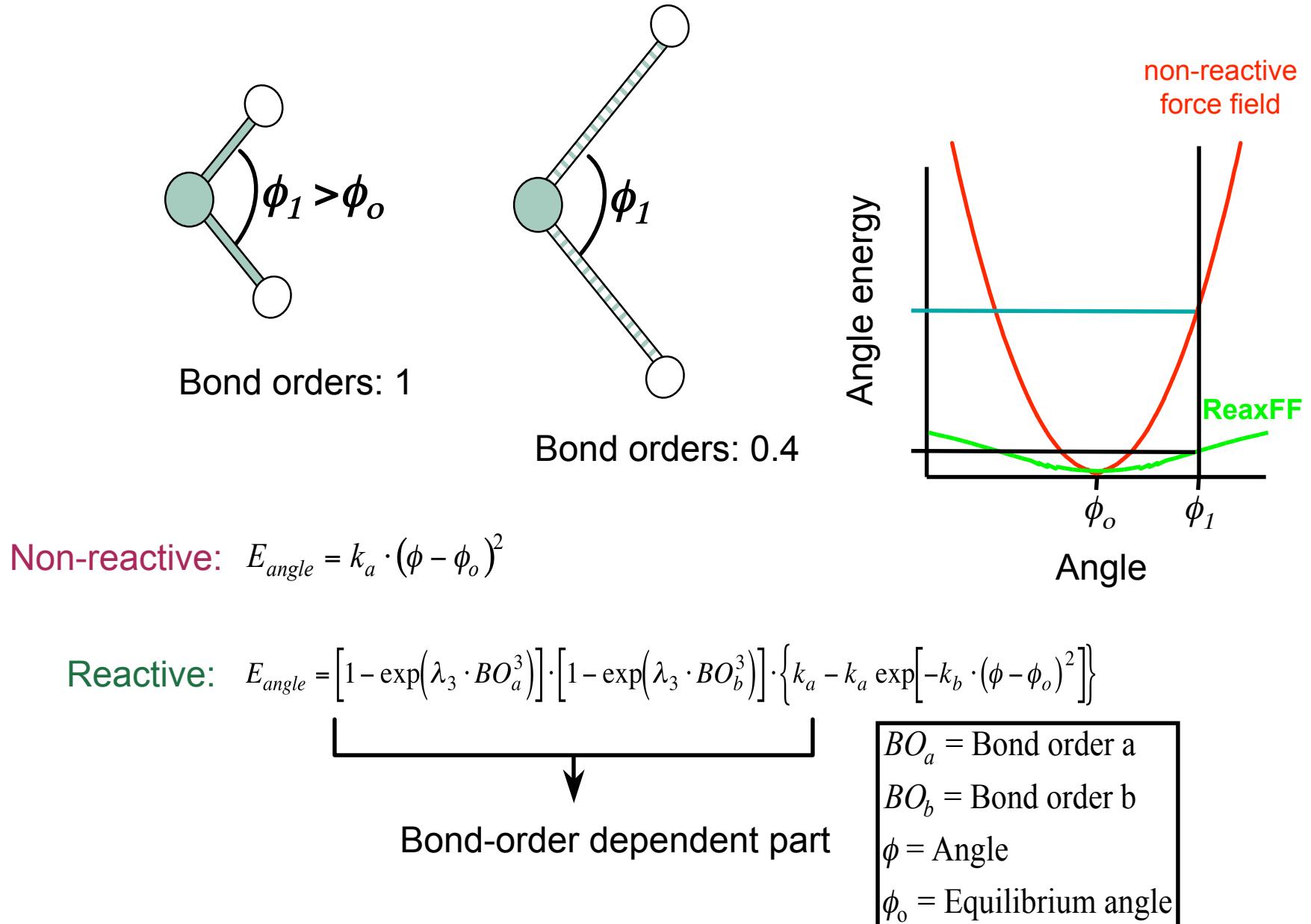
vdWaals: Shielded Morse potential

- 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), allowing ReaxFF to describe bulk metal

## Key features

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## Valence angles



# Torsion and conjugation

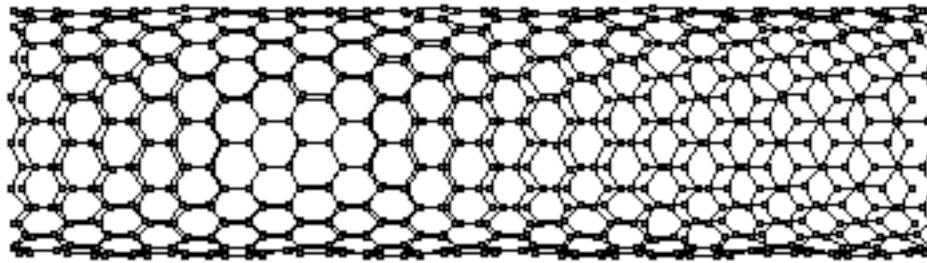
## - Torsion angle energy term

$$E_{tors} = f_{10}(BO_{ij}, BO_{jk}, BO_{kl}) \cdot \sin \Theta_{ijk} \cdot \sin \Theta_{jkl} \cdot \left[ \frac{1}{2} V_1 \cdot (1 + \cos \omega_{ijkl}) + \frac{1}{2} V_2 \cdot \exp \left\{ p_{tor1} \cdot (2 - BO_{jk}^\pi - f_{11}(\Delta_j, \Delta_k))^2 \right\} \cdot (1 - \cos 2\omega_{ijkl}) + \frac{1}{2} V_3 \cdot (1 + \cos 3\omega_{ijkl}) \right]$$

## - 4-body (torsion) conjugation term

$$E_{conj} = f_{12}(BO_{ij}, BO_{jk}, BO_{kl}) \cdot p_{cot1} \cdot [1 + (\cos^2 \omega_{ijkl} - 1) \cdot \sin \Theta_{ijk} \cdot \sin \Theta_{jkl}]$$

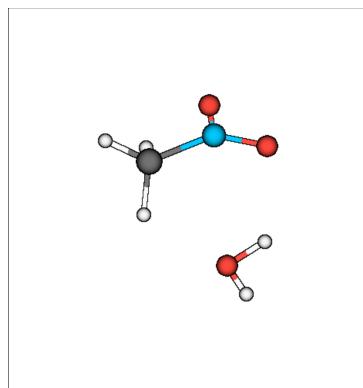
- Bond order dependent
- Tested against a large database of PAH heats of formation



ReaxFF simulation os stress-failure of a17\_0 nanotube

## - 3-body (angle) conjugation term

$$E_{coa} = p_{coa1} \cdot \frac{1}{1 + \exp(p_{coa2} \cdot \Delta_j^{val})} \cdot \exp \left[ -p_{coa3} \cdot \left( -BO_{ij} + \sum_{n=1}^{neighbours(i)} BO_{in} \right)^2 \right] \cdot \exp \left[ -p_{coa3} \cdot \left( -BO_{jk} + \sum_{n=1}^{neighbours(i)} BO_{kn} \right)^2 \right] \cdot \exp \left[ -p_{coa4} \cdot (BO_{ij} - 1.5)^2 \right] \cdot \exp \left[ -p_{coa4} \cdot (BO_{jk} - 1.5)^2 \right]$$



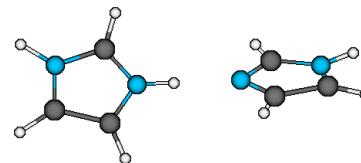
- Enables ReaxFF to describe of -NO<sub>2</sub>-group chemistry

ReaxFF simulation of H<sub>2</sub>O-catalyzed hydrogen shift in nitromethane

# Hydrogen bonds

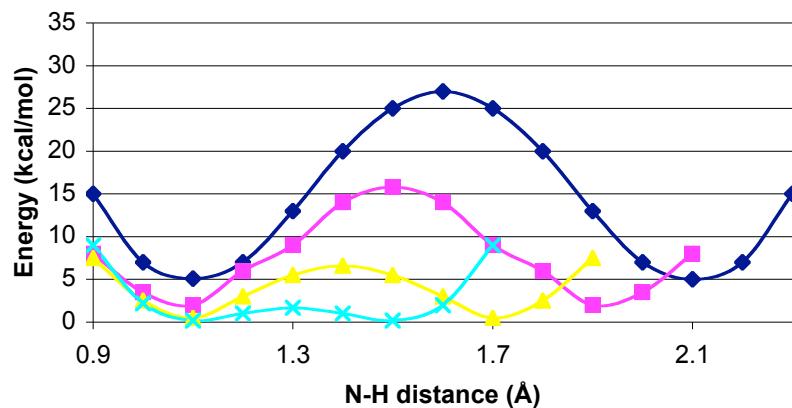
$$E_{Hbond} = p_{hb1} \cdot [1 - \exp(p_{hb2} \cdot BO_{XH})] \cdot \exp\left[p_{hb3} \left(\frac{r_{hb}^o}{r_{HZ}} + \frac{r_{HZ}^o}{r_{hb}^o} - 2\right)\right] \cdot \sin^8\left(\frac{\Theta_{XHZ}}{2}\right)$$

- N-N 3.2 Å
- N-N 3.0 Å
- ▲ N-N 2.8 Å
- \* N-N 2.6 Å

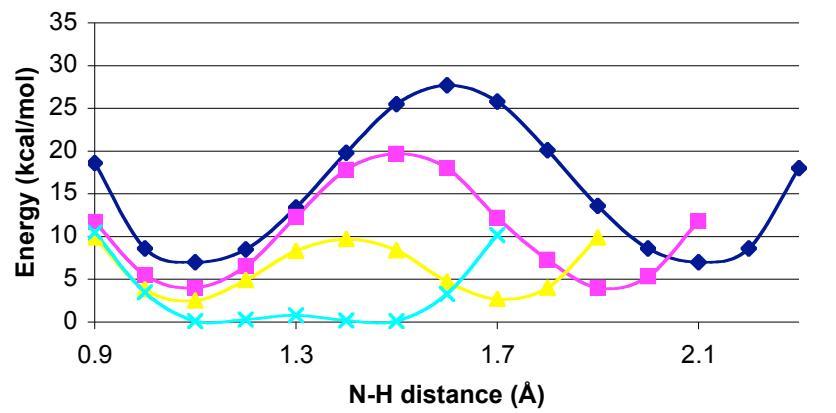


- Bond order dependent
- Tested for a wide range of hydrogen transfer reactions
- Recently started testing for liquid bulk phases

H-transfer in [Im-Im]<sup>+</sup>: QM-data



H-transfer in [Im-Im]<sup>+</sup>: ReaxFF-data



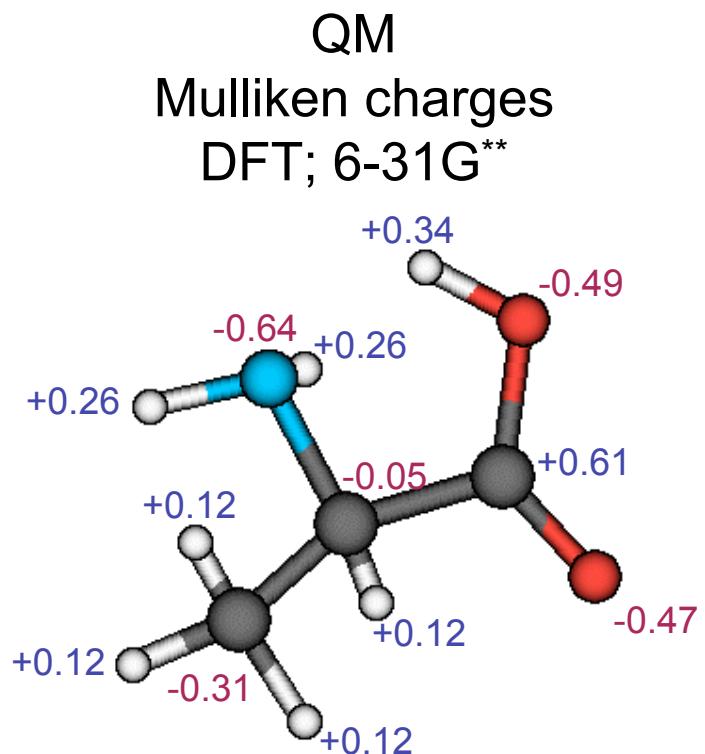
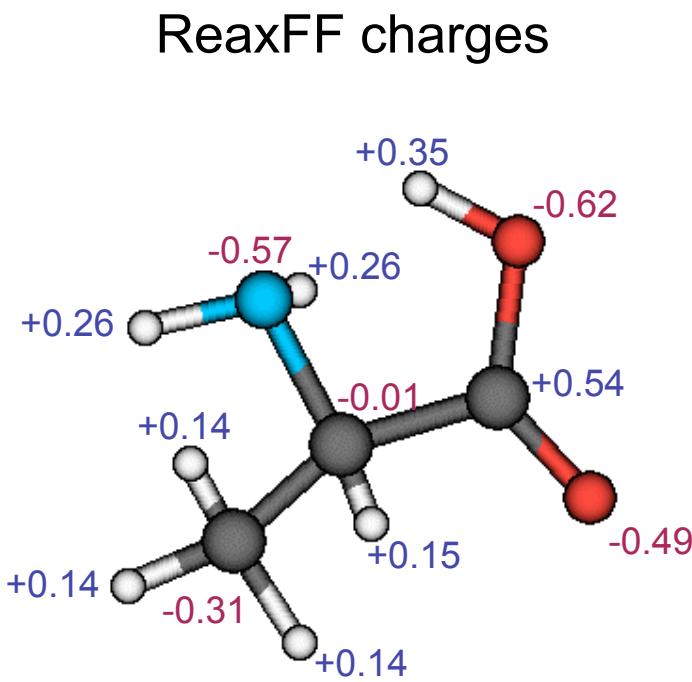
- Not yet included in pressure calculation

## Key features

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- ReaxFF uses a geometry-dependent charge calculation scheme that accounts for polarization effects.

## Charge calculation

- 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

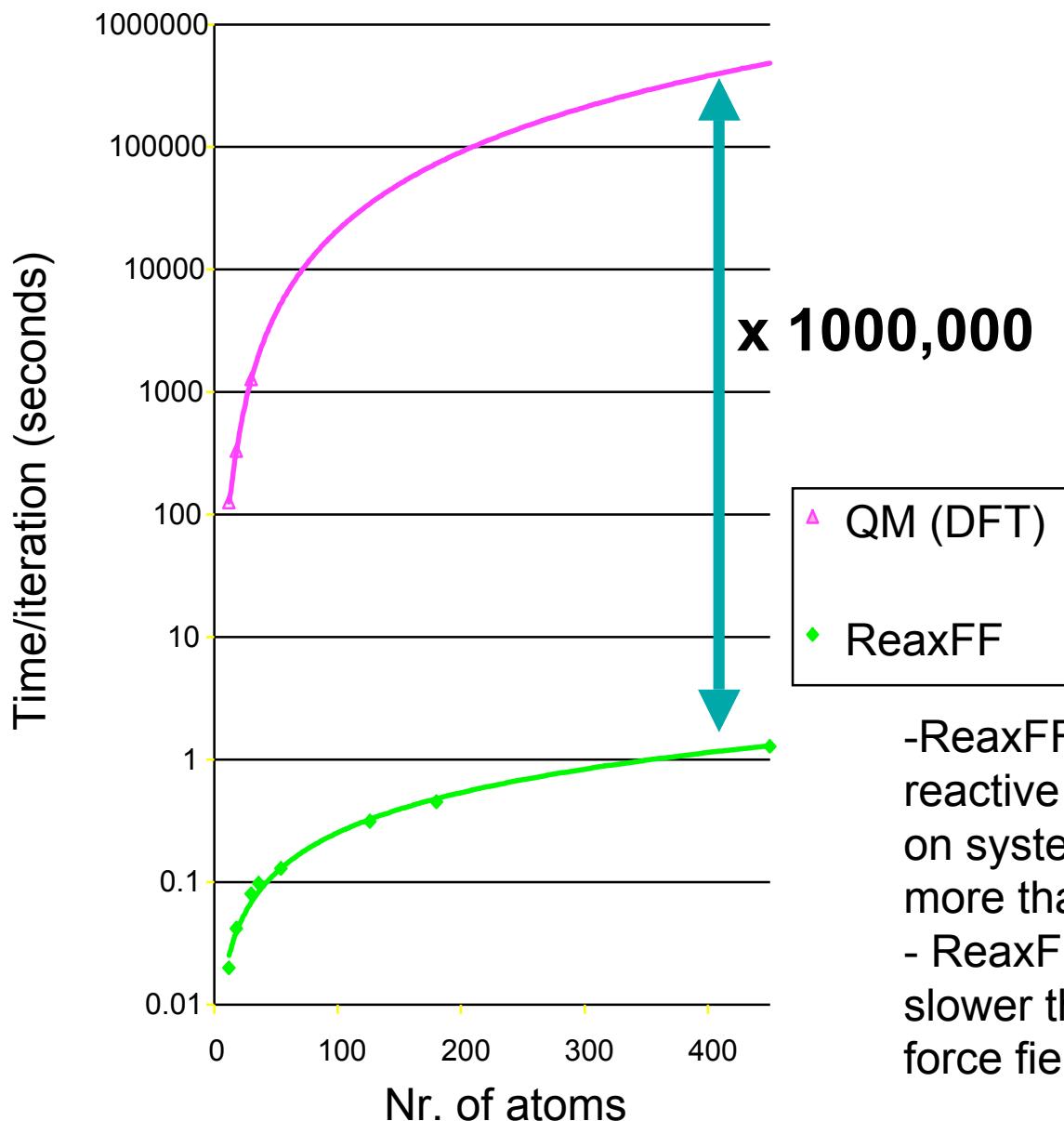


- ReaxFF properly describes the influence of chemical environment on atomic charge distribution

## General rules

- MD-force field; no discontinuities in energy or forces even during reactions.
- User should not have to pre-define reactive sites or reaction pathways; potential functions should be able to automatically handle coordination changes associated with reactions.
- Each element is represented by only 1 atom type in the force field; force field should be able to determine equilibrium bond lengths, valence angles etc. from chemical environment.

# ReaxFF Computational expense

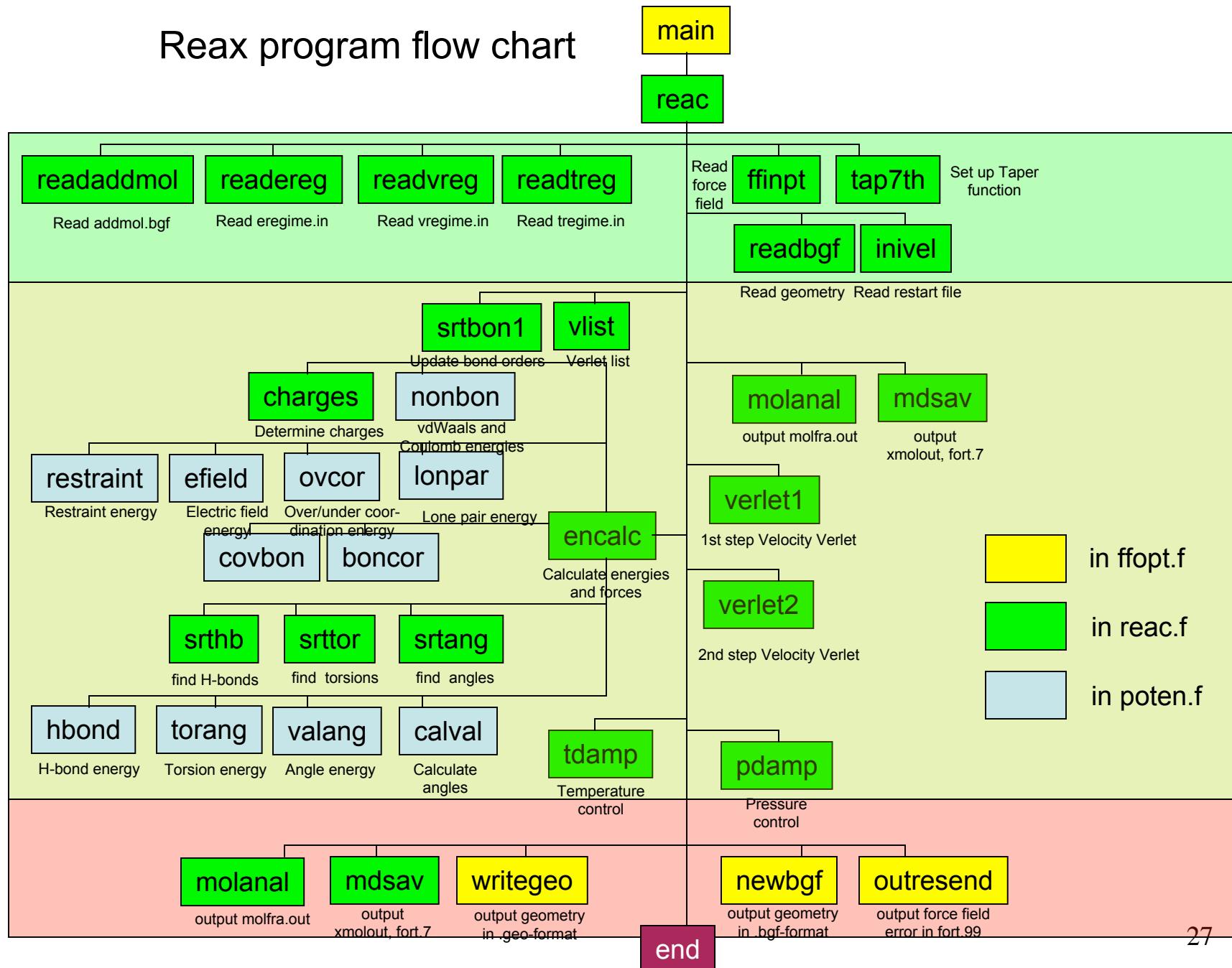


- ReaxFF allows for reactive MD-simulations on systems containing more than 1000 atoms
- ReaxFF is 10-50 times slower than non-reactive force fields

## 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

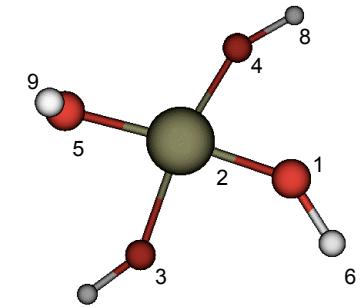
## General

### 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	BIOGRF 200 DESCRP ZrOH4	
Atom types and cartesian coordinates	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)<sub>4</sub>-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 BaZrO<sub>3</sub>\_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

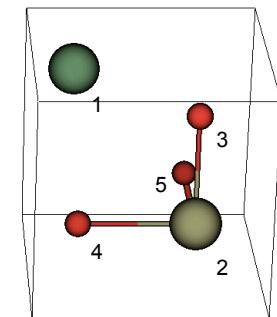
FORMAT CONECT (a6,12i6)

CONECT	1	2	2	2	2	2	2	2	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



BaZrO<sub>3</sub>-crystal

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

# control-file

```

# General parameters
 1 imetho
 1 igeofo
80.000 axis1
80.000 axis2
80.000 axis3
0.0050 cutoff2
0.300 cutoff3
 3 icharg
25 irecon
 0 ixmolo

# MD-parameters
 1 imdmet
0.250 tstep
0100.00 mdtemp
 2 itdmet
 1.0 tdamp1
0000.00 mdpres
00100.0 pdampl
0001000 nmdit
 00001 ichupd
   001 iout1
  0050 iout2
    1 iravel
001000 iout6
 000025 irten

# MM-parameters
2.00000 endmm
-000001 imaxmo
 00100 imaxit
1.00050 celopt
   0 icelo2

# FF-opt parameters
 0.0100 parext
   0 icelop
   1 igeopt

```

0: Normal MD-run 1: Energy minimisation 2:MD-energy minimisation  
0:xyz-input geometry 1: Biograf input geometry 2: xmol-input geometry  
a (for non-periodical systems)  
b (for non-periodical systems)  
c (for non-periodical systems)  
BO-cutoff for valency angles and torsion angles  
BO-cutoff for bond order for graphs  
Charges. 1:EEM 2:- 3: Shielded EEM 4: Full system EEM  
Frequency of reading control-file  
0: only x,y,z-coordinates in xmolout 1: molnr. in xmolout

MD-method. 1:Velocity Verlet+Berendsen 2:Hoover-Nose;3:NVE 4: NPT  
MD-time step (fs)  
1st MD-temperature  
0: T-damp atoms 1: Energy cons 2:System 3: Mols 4: Anderson  
1st Berendsen/Anderson temperature damping constant (fs)  
MD-pressure (MPa)  
Berendsen pressure damping constant (fs)  
Number of MD-iterations  
Charge update frequency  
Output to unit 71 and unit 73  
Save coordinates  
1: Random initial velocities  
Save velocity file  
Frequency of removal of rotational and translational energ

End point criterium for MM energy minimisation  
> 0: Maximum movement 0: Conjugate gradient < 0: MD-minimization  
Maximum number of iterations  
Cell parameter change  
Change all cell parameters (0) or only x/y/z axis (1/2/3)

Parameter optimization: extrapolation  
0: No cell parameter optimisation 1:Cell parameter optimisation  
0: Always use same start geometries 1:Use latest geometries

Parameter description  
(ignored by Reax)

Parameter  
value

Parameter  
name

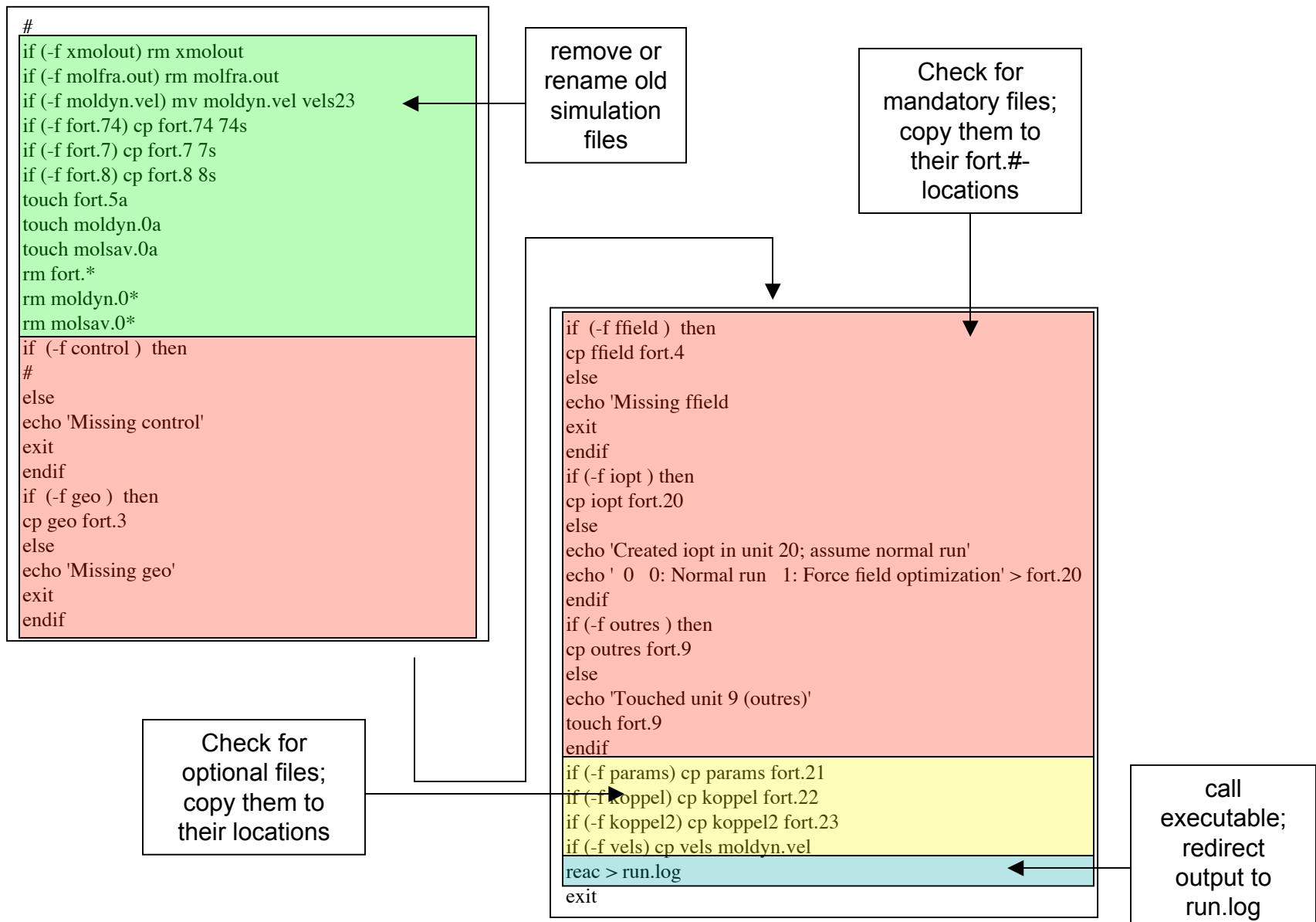
- lines can be organised in any order
- left-out keywords are given default value (see Manual)
- Beware: control-file is read during simulations**

# ffield-file

Reactive force field for hydrocarbons									
39 !Number of general parameters 2.1365 !Valency angle conjugation parameter 0.6991 !Overcoordination parameter 1.2593 !Overcoordination parameter 1.8512 !Valency/lone pair parameter ..... ..... 0.0000 !Molecular energy (not used) 2.6962 !Valency angle conjugation parameter									
2 !Nr of atoms; cov.r; valency;a.m;Rvdw;Evdw;gammaEEM;cov.r2;# alfa;gammavdW;valency;Eunder;Eover;chiEEM;etaEEM;n.u. cov r3;Elp;Heat inc.;n.u.;n.u.;n.u.;n.u. ov/un;val1;n.u.;val3,vval4									
C 1.3644 4.0000 12.0000 1.9803 0.1720 0.8712 1.2395 4.0000 9.4734 2.1241 4.0000 31.8793 79.5548 5.7254 ← 6.9235 0.0000 1.2636 0.0000 -0.0537 5.7133 33.5629 11.9957 0.8563 0.0000 -2.8983 4.7820 1.0564 4.0000 2.9663 0.0000 0.0000 0.0000									
H 0.6853 1.0000 1.0080 1.3588 0.0622 0.7625 -0.1000 1.0000 9.3992 5.0518 1.0000 0.0000 121.1250 3.8196 9.8832 1.0000 -0.1000 0.0000 -0.1609 3.8654 3.2462 1.0000 1.0698 0.0000 -15.7683 3.3504 1.0338 1.0000 2.8793 0.0000 0.0000 0.0000									
3 !Nr of bonds; Edis1;LPpen;n.u.;pb1;pb05;13corr;pb06 pbe2;pb03;pb04;n.u.;pb01;pb02;ovcorr									
1 1 139.8093 110.6913 77.2102 0.2737 -0.7584 1.0000 38.4226 0.3288 0.1235 -0.2010 8.6973 1.0000 -0.1042 6.1688 1.0000 0.0000									
1 2 159.8520 0.0000 0.0000 -0.4646 0.0000 1.0000 6.0000 0.6170 12.3878 1.0000 0.0000 1.0000 -0.0098 8.5954 0.0000 0.0000									
2 2 170.0433 0.0000 0.0000 -0.3573 0.0000 1.0000 6.0000 0.7489 9.6471 1.0000 0.0000 1.0000 -0.0169 5.8818 0.0000 0.0000									
1 !Nr of off-diagonal terms; Ediss;Ro;gamma;rsigma;rpi:rpi2									
1 2 0.0431 1.7204 10.3632 1.0386 -1.0000 -1.0000									
3 !Nr of angles;at1;at2;at3;Thetao,o;ka;kb;pvl;pv2									
1 1 1 75.8304 33.9168 0.8043 0.0000 0.1780 10.5736 1.0400 1 1 2 69.6421 9.2578 3.6521 0.0000 0.0058 0.0000 1.0400									
2 1 2 75.4958 14.5436 2.7438 0.0000 0.0127 0.0000 1.0400									
3 !Nr of torsions;at1;at2;at3;at4;;V1;V2;V3;V2(BO);vconj;n.u;n									
1 1 1 1 0.0000 38.9174 0.3649 -8.2931 -2.0127 0.0000 0.0000 1 1 1 2 0.0000 49.1001 0.2713 -8.5284 -1.5309 0.0000 0.0000									
2 1 1 2 0.0000 34.0265 0.3804 -6.3917 -0.9965 0.0000 0.0000									

- 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)

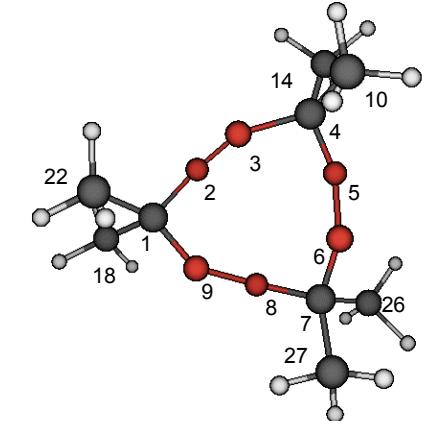
Atom number	Connection table				Bond orders					Number of lone pairs			
33. TATP	1	1	2	9	18	22	0	1	0.053	1.098	0.974	0.963	0.000
	2	3	1	3	0	0	0	1	1.053	0.751	0.000	0.000	0.000
	3	3	2	4	0	0	0	1	0.751	0.935	0.000	0.000	0.000
	4	1	3	5	10	14	0	1	0.935	1.133	0.959	1.002	0.000
	5	3	4	6	0	0	0	1	1.133	0.578	0.000	0.000	0.000
	6	3	5	7	0	0	0	1	0.578	1.071	0.000	0.000	0.000
	7	1	6	8	26	27	0	1	1.071	1.046	1.001	0.983	0.000
	8	3	7	9	0	0	0	1	1.046	0.646	0.000	0.000	0.000
	9	3	1	8	0	0	0	1	1.098	0.646	0.000	0.000	0.000
	10	1	4	11	12	13	0	1	0.959	0.971	0.981	0.978	0.000
	11	2	10	0	0	0	0	1	0.971	0.000	0.000	0.000	0.000
	12	2	10	0	0	0	0	1	0.981	0.000	0.000	0.000	0.000
	13	2	10	0	0	0	0	1	0.978	0.000	0.000	0.000	0.000
	14	1	4	15	16	17	0	1	1.002	0.977	0.973	0.987	0.000
	15	2	14	0	0	0	0	1	0.977	0.000	0.000	0.000	0.000
	16	2	14	0	0	0	0	1	0.973	0.000	0.000	0.000	0.000
	17	2	14	0	0	0	0	1	0.987	0.000	0.000	0.000	0.000
	18	1	1	19	20	21	0	1	0.974	0.982	0.981	0.973	0.000
	19	2	18	0	0	0	0	1	0.982	0.000	0.000	0.000	0.000
	20	2	18	0	0	0	0	1	0.981	0.000	0.000	0.000	0.000
	21	2	18	0	0	0	0	1	0.973	0.000	0.000	0.000	0.000
	22	1	1	23	24	25	0	1	0.963	0.980	0.981	0.983	0.000
	23	2	22	0	0	0	0	1	0.980	0.000	0.000	0.000	0.000
	24	2	22	0	0	0	0	1	0.981	0.000	0.000	0.000	0.000
	25	2	22	0	0	0	0	1	0.983	0.000	0.000	0.000	0.000
	26	1	7	28	29	30	0	1	1.001	0.975	0.967	0.985	0.000
	27	1	7	31	32	33	0	1	0.983	0.986	0.976	0.987	0.000
	28	2	26	0	0	0	0	1	0.975	0.000	0.000	0.000	0.000
	29	2	26	0	0	0	0	1	0.967	0.000	0.000	0.000	0.000
	30	2	26	0	0	0	0	1	0.985	0.000	0.000	0.000	0.000
	31	2	27	0	0	0	0	1	0.986	0.000	0.000	0.000	0.000
	32	2	27	0	0	0	0	1	0.976	0.000	0.000	0.000	0.000
	33	2	27	0	0	0	0	1	0.987	0.000	0.000	0.000	0.000
									63.9132746	12.	87.9132747	1.98401163E-06	

Atom type

Molecule number

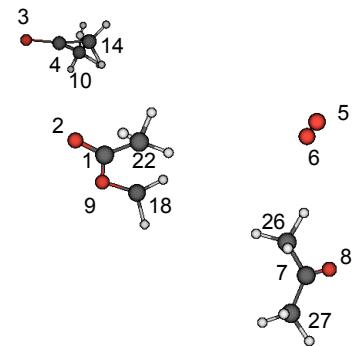
Total bond order

Charge

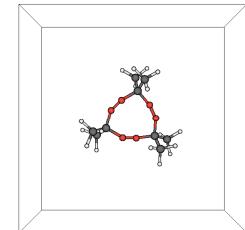


## Trajectory (xmolout)

Nr. of atoms		Iteration		Trajectory (xmolout)							
	33		50000	-3263.2723	15.00	15.00	15.00	90.00	90.00	90.00	
	TATP										
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	12.0255	1.43429	4							



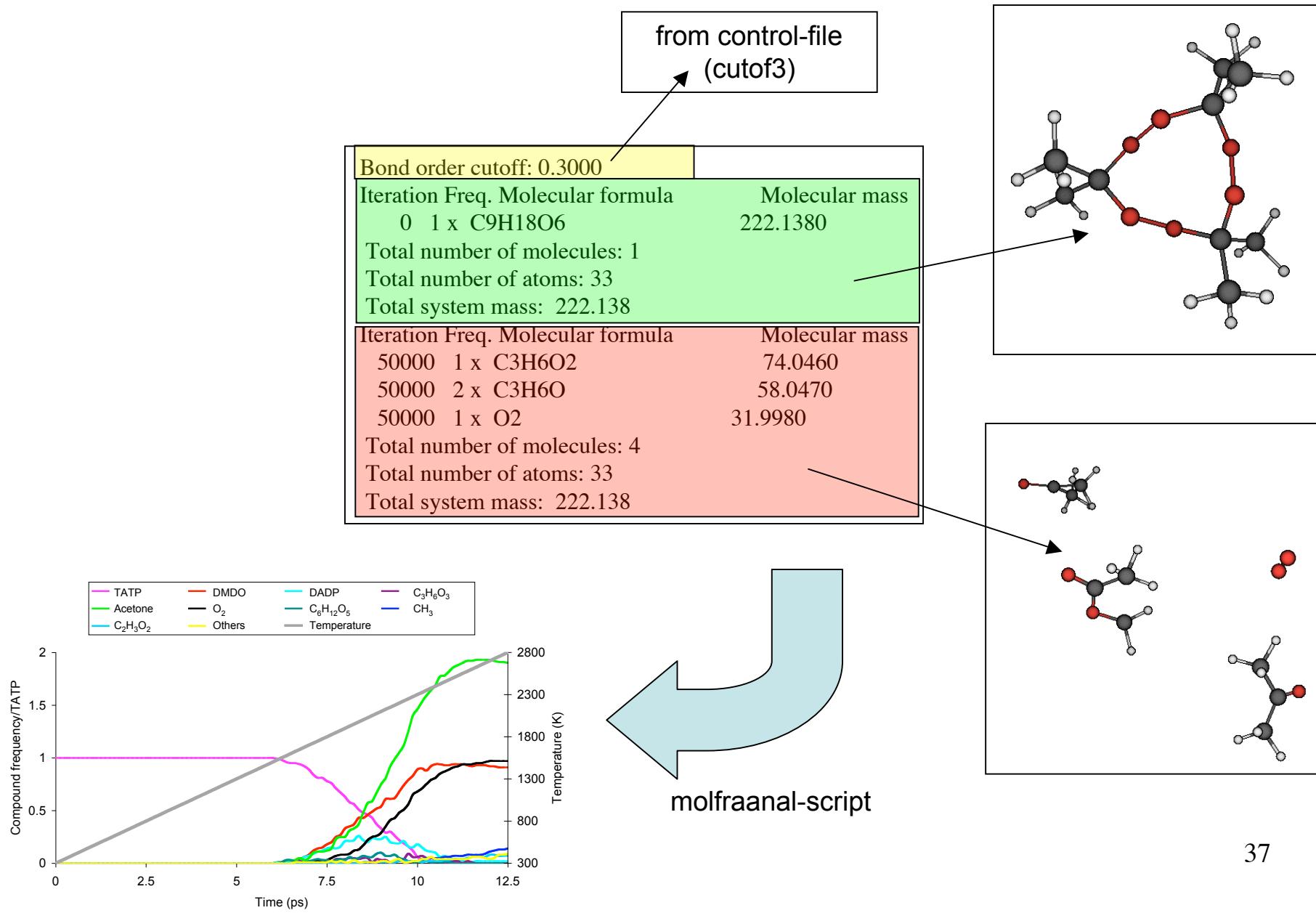
O<sub>2</sub>, 2 acetone  
and 1 C<sub>3</sub>H<sub>5</sub>O<sub>2</sub>



# xmol2ppm-script

- viewable in molden, vmd, Xmol, etc.

# Molecular composition (molfra.out)



## 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

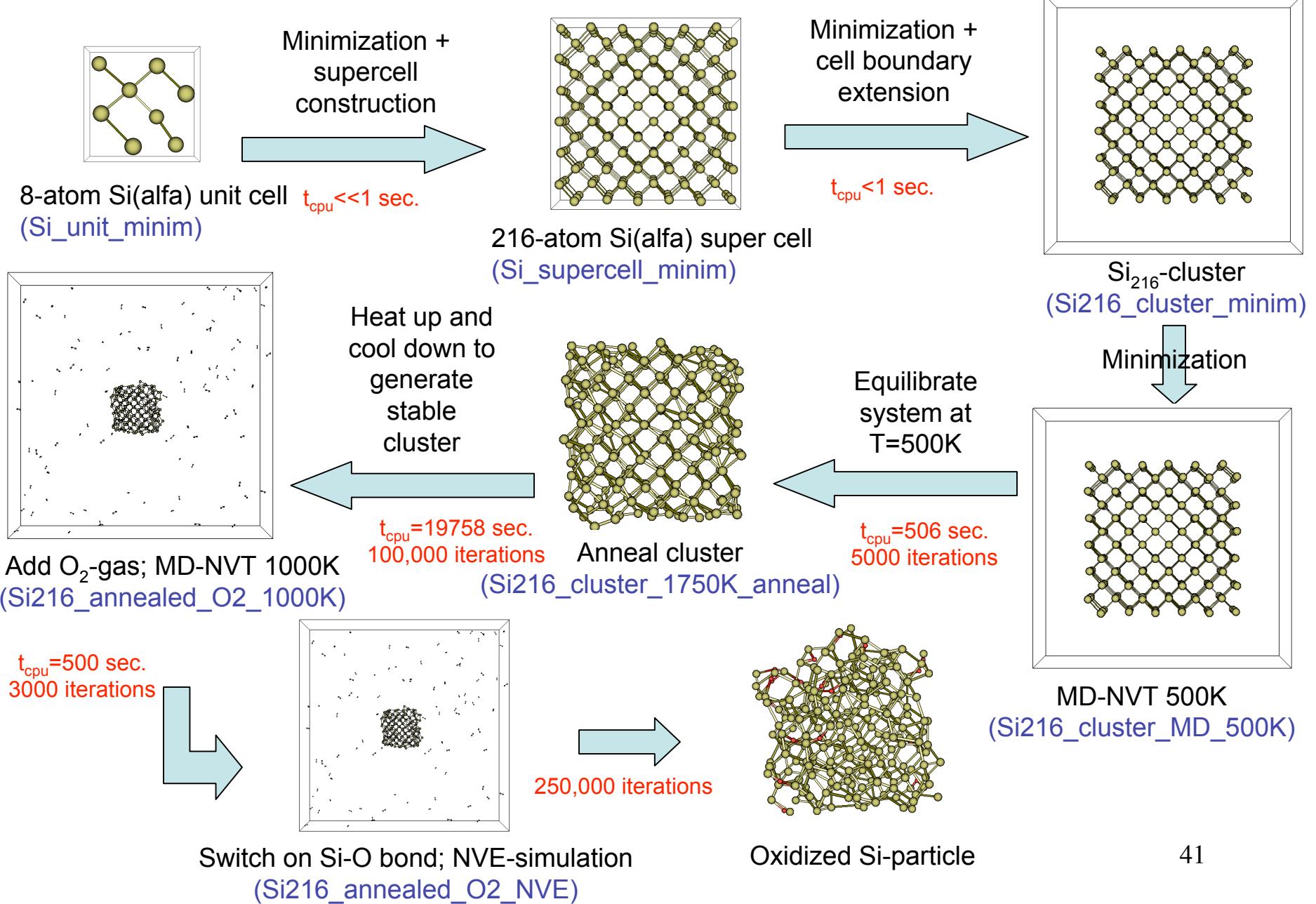
**fort.58-file: partial energies**

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

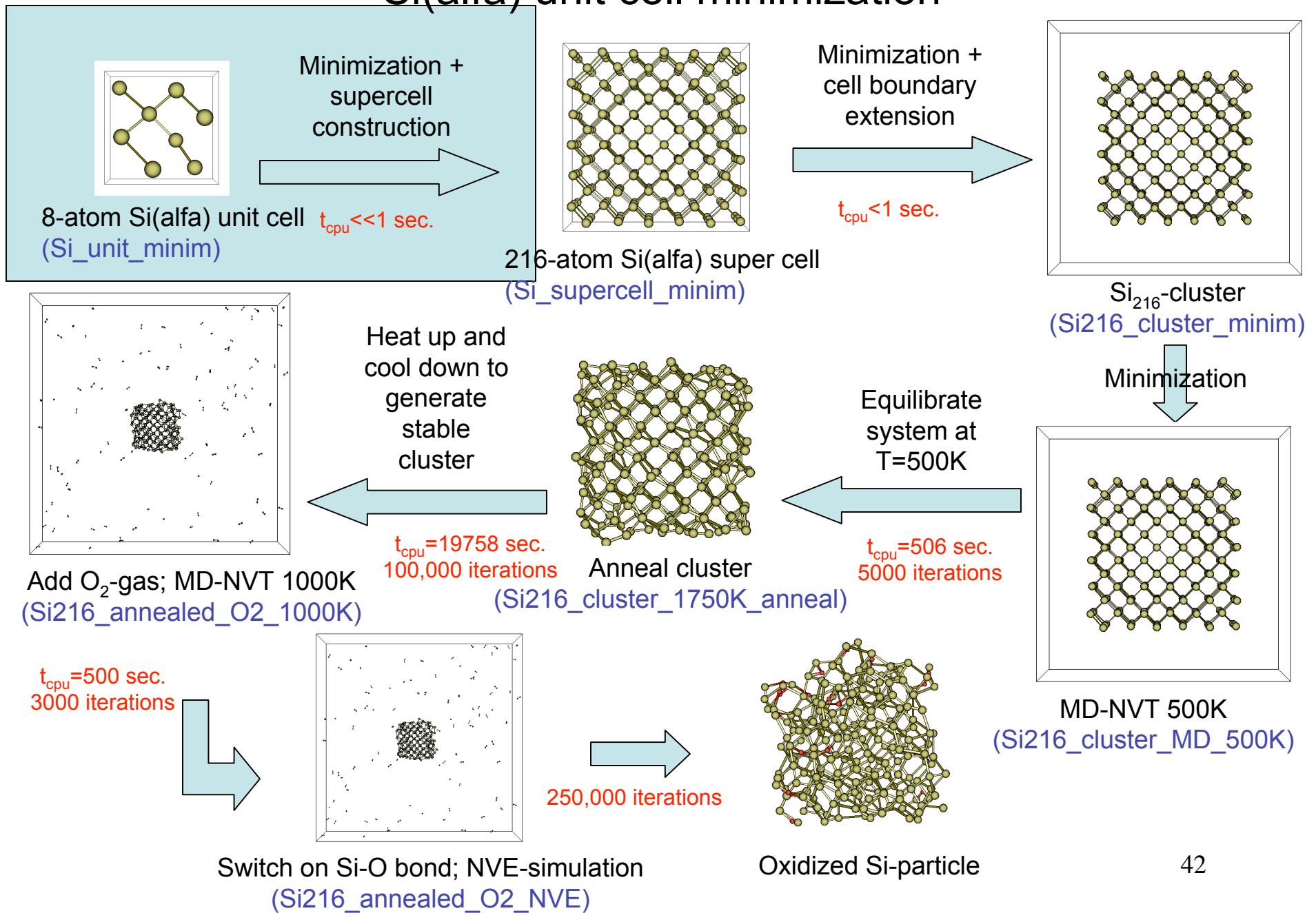
# Examples

- Si particle oxidation
  - Si-unit cell minimization
  - Creation of a 216-atom supercell
  - Creation of a  $\text{Si}_{216}$ -cluster
  - $\text{Si}_{216}$ -equilibration at  $T=500\text{K}$
  - MD-anneal simulation of  $\text{Si}_{216}$ -cluster
  - Addition of  $\text{O}_2$ : equilibration at  $T=1000\text{K}$
  - NVE-simulation of  $\text{Si}_{216}$ -particle oxidation
- Si-surface impact on  $\text{SiO}_2/\text{Si}$
- Force field development

# Si-particle oxidation



# Si(alfa) unit cell minimization



# Input files

```

XTLGRF 200
DESCRP a_Si_opt
REMARK BGF file created by Cerius2
CRYSTX 5.37054 5.37054 5.37054 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      2.21392 4.69918 4.69918 Si 1 1 0.00000
HETATM 2 Si      3.35661 3.35665 0.67137 Si 1 1 0.00000
HETATM 3 Si      4.69919 4.69918 2.01387 Si 1 1 0.00000
HETATM 4 Si      3.35661 0.87138 3.35666 Si 1 1 0.00000
HETATM 5 Si      2.01392 2.01387 2.01387 Si 1 1 0.00000
HETATM 6 Si      0.67135 3.35665 3.35665 Si 1 1 0.00000
HETATM 7 Si      4.69919 2.21387 4.69918 Si 1 1 0.00000
HETATM 8 Si      0.47135 0.67137 0.67137 Si 1 1 0.00000
FORMAT CONECT (a6,12i6)
CONECT 1 2 4 6 8
CONECT 2 1 3 5 7
CONECT 3 2 4 6 8
CONECT 4 1 3 5 7
CONECT 5 2 4 6 8
CONECT 6 1 3 5 7
CONECT 7 2 4 6 8
CONECT 8 1 3 5 7
UNIT ENERGY kcal
ENERGY -840.102370
END

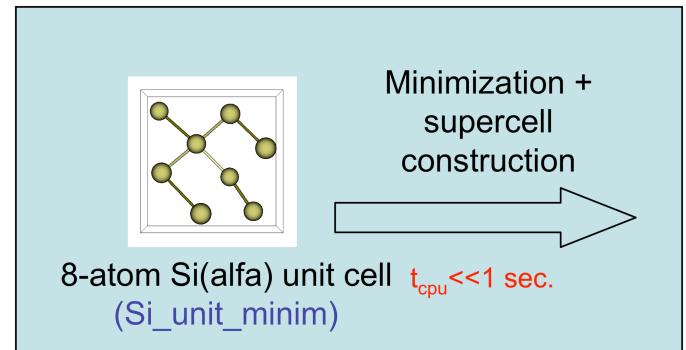
```

**geo**

# General parameters	Relevant keyword
2 <b>iexx</b> Nr. of unit cells in x-direction to fort.85	Default keyword
2 <b>iexy</b> Nr. of unit cells in y-direction to fort.85	
2 <b>iexz</b> Nr. of unit cells in z-direction to fort.85	
1 <b>icentr</b> 0: use user definitions 1: place system in centre periodic box 2: place...	
1 <b>itrans</b> 0: do not back-translate atoms 1: Translate atoms after crossing....	
02.50 range Range for back-translation of atoms	
1 <b>imetho</b> 0: Normal MD-run 1: Energy minimisation	
1 <b>igeofo</b> 0:xyz-input geometry 1: Biograf input geometry 2: xmol-input geometry	
...	
# MD-parameters	
...	
...	
# MM-parameters	
0.25000 <b>endmm</b> End point criterium for MM energy minimisation	
00000 <b>imaxmo</b> <0: MD-minimization > 0 Steepest descent 0: Conjugate gradient	
00100 <b>imaxit</b> Maximum number of iterations	
100 <b>iout4</b> Frequency of structure output during minimisation	
0 <b>iout5</b> 1:Remove fort.57 and fort.58 files	
1.0010 <b>celopt</b> Cell parameter change	

**control**

- Other input files : exe, ffield (standard)



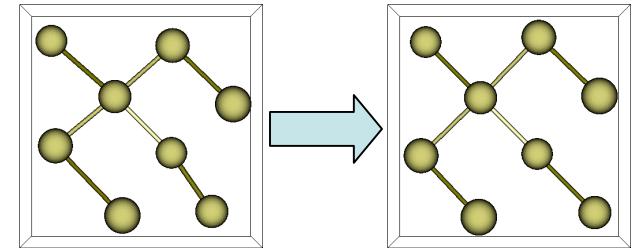
# Output files

a\_Si\_opt

Iter.	Epot	Max.move	Factor	RMSG	nfc
0	-736.9644800470	0.000000	0.500000	35.921660	0
1	-822.5463965951	140.063487	249.509895	14.456718	0
2	-836.1836232543	51.604572	0.439696	5.823455	0
3	-838.4628016697	0.037037	1.183627	2.997409	0
4	-839.8757995658	0.024440	2.485671	2.064547	0
5	-840.0985306099	0.016776	0.979394	0.240787	0

Minimization report

fort.57



F a\_Si\_opt

```

16.1116 16.1116 16.1116
90.0000 90.0000 90.0000
1 Si  0.201308156929372E+01 0.469899935734249E+01 0.469807931385440E+01
2 Si  0.335759198919583E+01 0.335587406316292E+01 0.670911888011277E+00
3 Si  0.470033249708392E+01 0.469958237639442E+01 0.201445663138070E+01
4 Si  0.335777021158629E+01 0.672111934782872E+00 0.335650185775585E+01
5 Si  0.201204640419919E+01 0.201385656448758E+01 0.201417913836992E+01
6 Si  0.671235173288612E+00 0.335568198874663E+01 0.335689140989500E+01
7 Si  0.469992123632136E+01 0.201377860766508E+01 0.469916007001880E+01
...
...
208 Si 0.114112609190311E+02 0.114133546379105E+02 0.604251875169898E+01
209 Si 0.127541615692937E+02 0.154400788878349E+02 0.154391583748393E+02
210 Si 0.140986719891958E+02 0.140969535936554E+02 0.114119909489962E+02
211 Si 0.154414124970839E+02 0.154406619068869E+02 0.127555356923656E+02
212 Si 0.140988502115863E+02 0.114131914652753E+02 0.140975809187408E+02
213 Si 0.127531264041992E+02 0.127549360949800E+02 0.127552581993549E+02
214 Si 0.114123151732886E+02 0.140967615192391E+02 0.140979704708799E+02
215 Si 0.154410012363213E+02 0.127548581381575E+02 0.154402391310037E+02
216 Si 0.114112609190311E+02 0.114133546379105E+02 0.114130587516990E+02

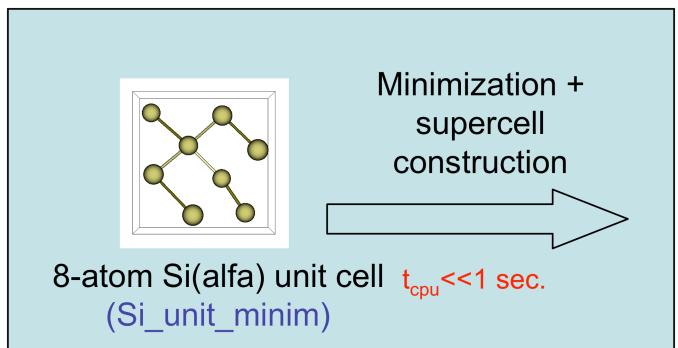
```

fort.85

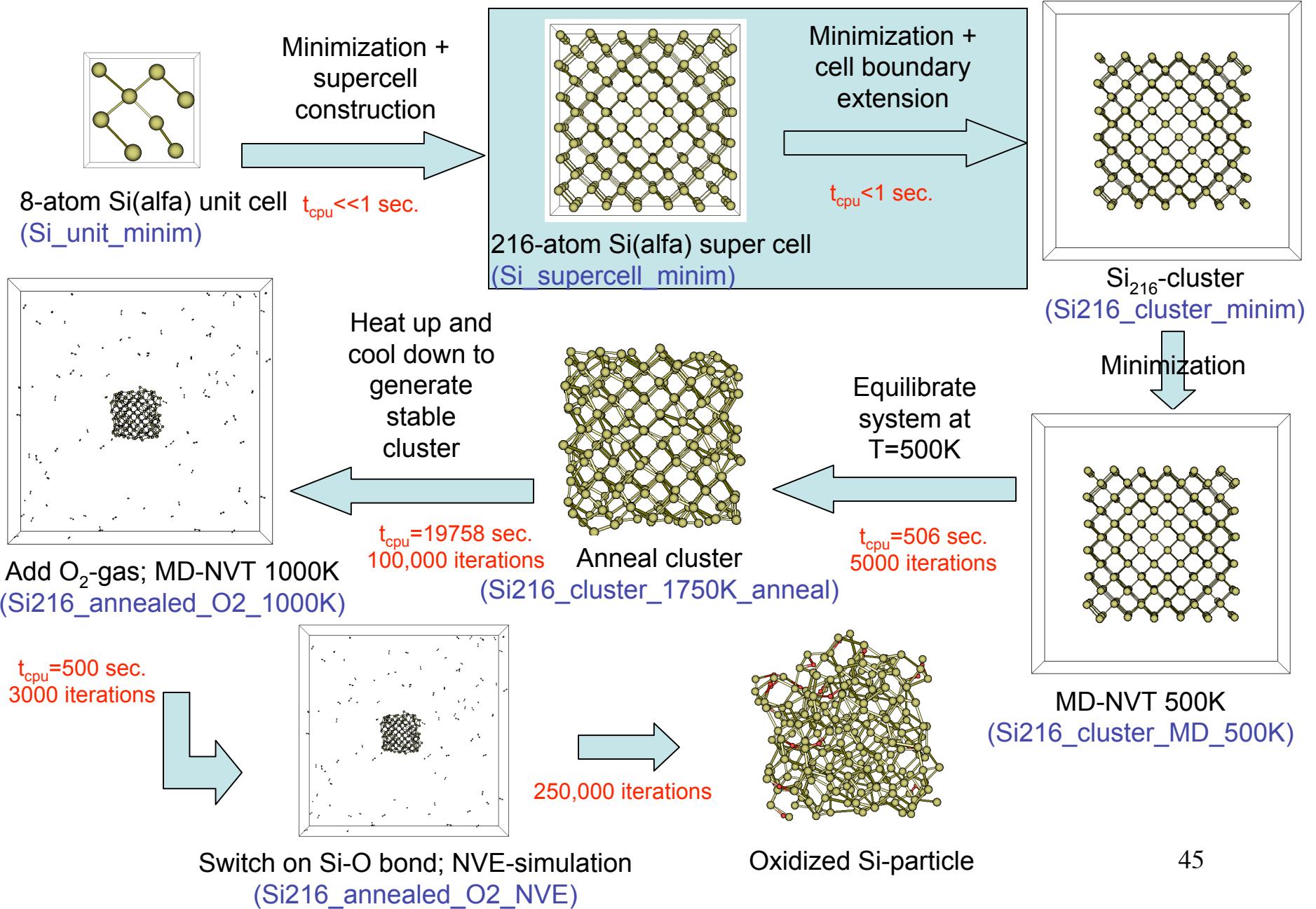
Extended unit cell (xyz-format)

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
- summary.txt: summary simulation



# 216-atom super cell minimization



# Input files

```
F a_Si_opt
16.1116 16.1116 16.1116
90.0000 90.0000 90.0000
1 Si 0.201308156929372E+01 0.469899935734249E+01 0.469807931385440E+01
2 Si 0.335759198919583E+01 0.335587406316292E+01 0.670911888011277E+00
3 Si 0.470033249708392E+01 0.469958237639442E+01 0.201445663138070E+01
4 Si 0.335777021158629E+01 0.672111934782872E+00 0.335650185775585E+01
5 Si 0.201204640419919E+01 0.201385656448758E+01 0.201417913836992E+01
6 Si 0.671235173288612E+00 0.335568198874663E+01 0.335689140989500E+01
7 Si 0.469992123632136E+01 0.201377860766508E+01 0.469916007001880E+01
...
...
208 Si 0.114112609190311E+02 0.114133546379105E+02 0.604251875169898E+01
209 Si 0.127541615692937E+02 0.154400788878349E+02 0.154391583748393E+02
210 Si 0.140986719891958E+02 0.140969535936554E+02 0.114119909489962E+02
211 Si 0.154414124970839E+02 0.154406619068869E+02 0.127555356923656E+02
212 Si 0.140988502115863E+02 0.114131914652753E+02 0.140975809187408E+02
213 Si 0.127531264041992E+02 0.127549360949800E+02 0.127552581993549E+02
214 Si 0.114123151732886E+02 0.140967615192391E+02 0.140979704708799E+02
215 Si 0.154410012363213E+02 0.127548581381575E+02 0.154402391310037E+02
216 Si 0.114112609190311E+02 0.114133546379105E+02 0.11430587516990E+02
```

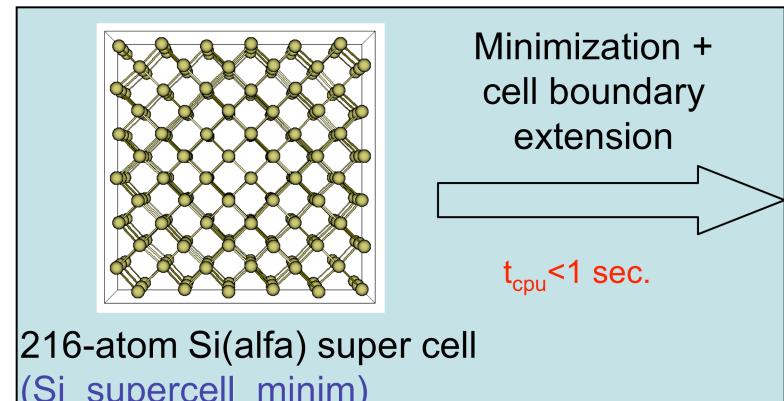
geo (fort.85)

```
# General parameters
 1 icentr 0: use user definitions 1: place system in centre periodic box 2: place...
 1 itrans 0: do not back-translate atoms 1: Translate atoms after crossing....
 02.50 range Range for back-translation of atoms
 1 imetho 0: Normal MD-run 1: Energy minimisation
 0 igeofo 0:xyz-input geometry 1: Biograf input geometry 2: xmol-input geometry
 ...
 ...
# MD-parameters
 ...
 ...
# MM-parameters
 0.25000 endmm End point criterium for MM energy minimisation
 00000 imaxmo <0: MD-minimization >0 Steepest descent 0: Conjugate gradient
 00100 imaxit Maximum number of iterations
   100 iout4 Frequency of structure output during minimisation
     0 iout5 1:Remove fort.57 and fort.58 files
 1.0010 celopt Cell parameter change
```

**Relevant keyword**  
**Default keyword**

control

- Other input files : exe, ffield (standard)



# Output files

a_Si_opt					
Iter.	Epot	Max.move	Factor	RMSG	nfc
0	-22682.6666450342	0.000000	0.500000	0.240736	0
1	-22682.7652811318	1.040171	1.821356	0.061526	0

fort.57

- Final energy exactly 27xunit cell energy
- No forces on supercell structure

## Minimization report

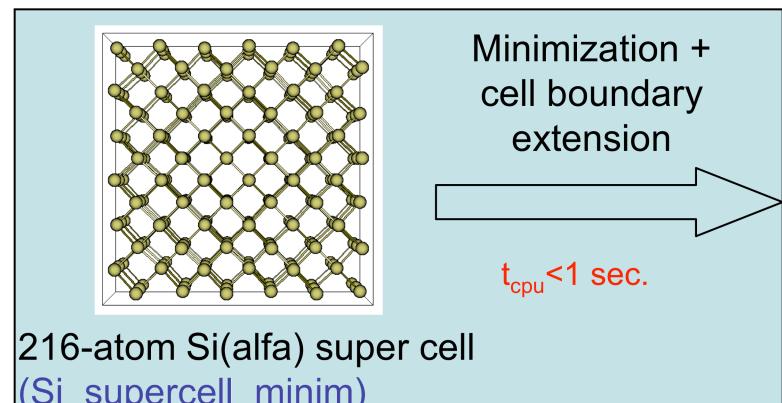
```
XTLGRF 200
DESCRP a_Si_opt
RUTYPE NORMAL RUN
CRYSTX 16.11160 16.11160 16.11160 90.00000 90.00000 90.00000
FORMAT ATOM (a6,1x,i5,1x,a5,1x,a3,1x,a1,1x,a5,3f10.5,1x,a5,i3,i2,1x,f8.5)
HETATM 1 Si      2.01390 4.69950 4.69915 Si 0 0 0.00000
HETATM 2 Si      3.35655 3.35653 0.67134 Si 0 0 0.00000
HETATM 3 Si      4.69957 4.69900 2.01424 Si 0 0 0.00000
HETATM 4 Si      3.35663 0.67166 3.35634 Si 0 0 0.00000
HETATM 5 Si      2.01386 2.01398 2.01394 Si 0 0 0.00000
...
...
END
```

fort.90

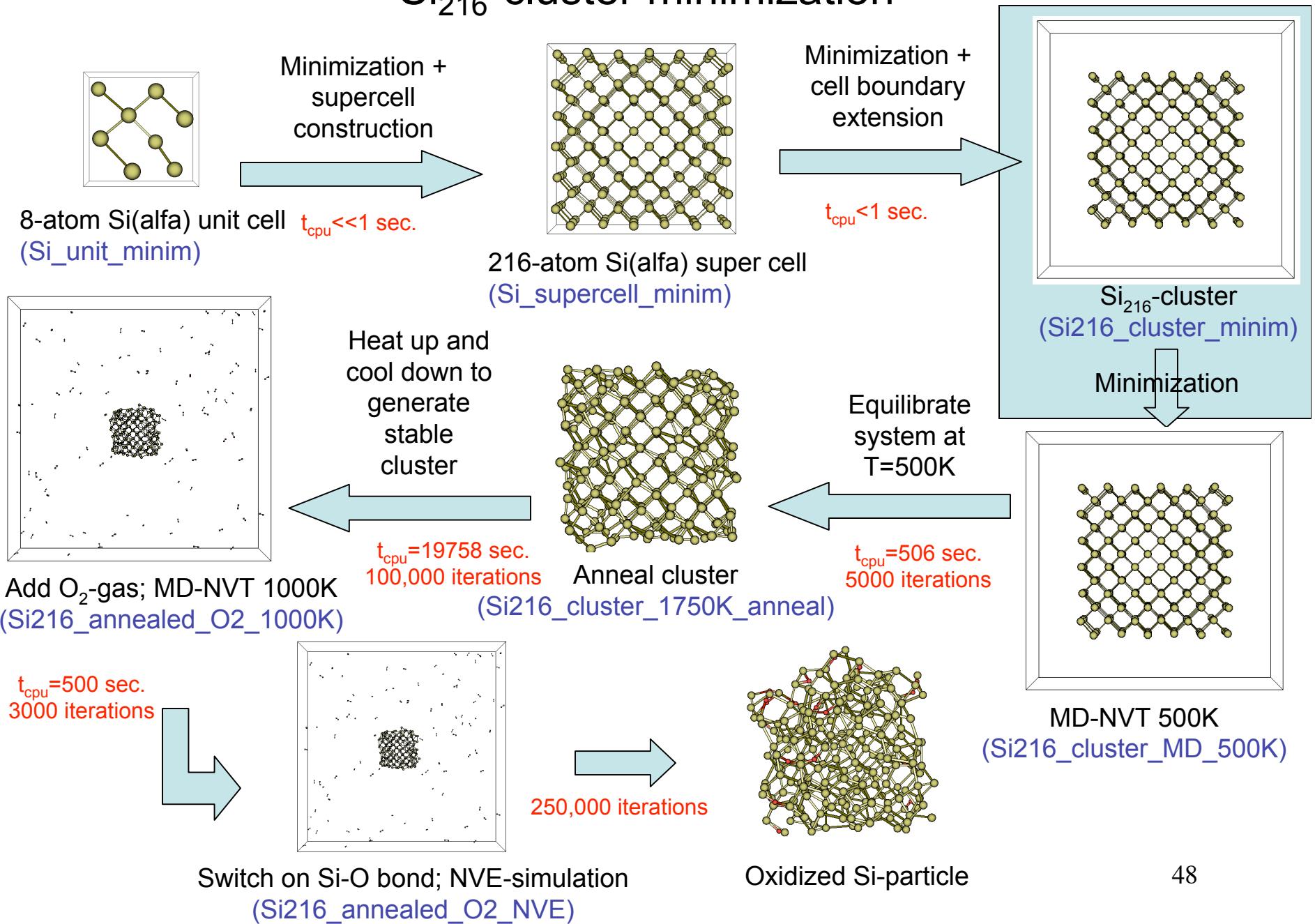
## Biograf output-file

### Other output files:

- fort.7, fort.8: connection table
- fort.58: partial energies
- fort.73: final partial energies
- xmolout: .xyz coordinates
- molfra.out : system composition
- summary.txt: summary simulation



# $\text{Si}_{216}$ -cluster minimization



# Input files

```
XTLGRF 200
DESCRP a_Si_opt
RUTYPE NORMAL RUN
CRYSTX 100.0000 100.0000 100.0000 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    2.01390 4.69950 4.69915 Si 0 0 0.00000
HETATM 2 Si    3.35655 3.35653 0.67134 Si 0 0 0.00000
HETATM 3 Si    4.69957 4.69900 2.01424 Si 0 0 0.00000
HETATM 4 Si    3.35663 0.67166 3.35634 Si 0 0 0.00000
HETATM 5 Si    2.01386 2.01398 2.01394 Si 0 0 0.00000
...
...
END
```

fort.90

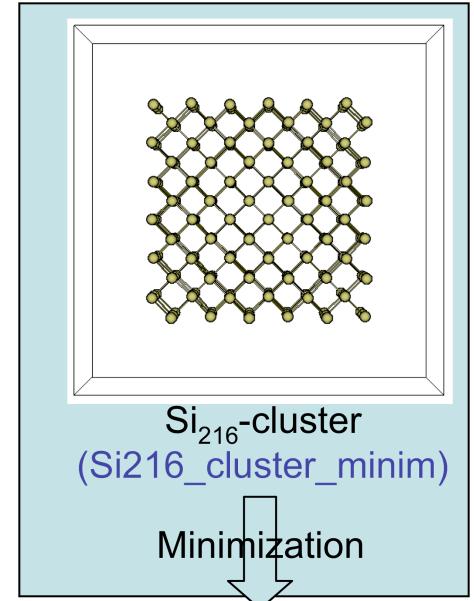
```
# General parameters
 1 icentr 0: use user definitions 1: place system in centre periodic box 2: place...
 1 itrans 0: do not back-translate atoms 1: Translate atoms after crossing....
02.50 range   Range for back-translation of atoms
 1 imetho 0: Normal MD-run 1: Energy minimisation
 0 igeof0 0:xyz-input geometry 1: Biograf input geometry 2: xmol-input geometry
 ...
 ...
# MD-parameters
 ...
 ...
# MM-parameters
0.25000 endmm End point criterium for MM energy minimisation
00000 imaxmo <0: MD-minimization >0 Steepest descent 0: Conjugate gradient
00100 imaxit Maximum number of iterations
 100 iout4 Frequency of structure output during minimisation
   0 iout5 1:Remove fort.57 and fort.58 files
1.0010 celopt Cell parameter change
```

Relevant keyword  
Default keyword

control

Biograf output-file; enlarged a,b,c-cell  
parameters

- Other input files : exe, ffield (standard)



# Output files

a_Si_opt						
Iter.	Epot	Max.move	Factor	RMSG	nfc	
0	-17559.9674767871	0.000000	0.500000	1.630894	0	
1	-17568.4636532682	8.006336	26.287993	1.236421	0	
2	-17574.4035079074	6.237768	0.124479	1.059034	0	
3	-17578.3600076452	0.011439	1.732245	0.835918	0	
4	-17581.0792461733	0.010239	1.735968	0.709652	0	
5	-17582.7576167442	0.009124	1.528955	0.552894	0	
6	-17583.6481598536	0.006785	1.278410	0.278725	0	
7	-17583.9871860266	0.003339	2.167157	0.336433	0	
8	-17584.6500727875	0.005791	2.483300	0.313884	0	
9	-17584.9022993227	0.005450	1.396609	0.175932	0	

fort.57

## Other output files:

- fort.58: partial energies
- fort.73: final partial energies
- xmolout: .xyz coordinates
- molfra.out : system composition
- summary.txt: summary simulation

Atom#	Connected atoms					Bond orders					#lone pairs				
..															
208	6	107	127	169	205	0	1	0.806	0.808	0.808	0.807	0.000	3.228	0.000	0.000
209	6	214	0	0	0	0	1	0.807	0.000	0.000	0.000	0.000	0.807	1.021	0.000
210	6	201	207	211	213	0	1	0.807	0.807	0.808	0.807	0.000	3.229	0.000	0.000
211	6	210	0	0	0	0	1	0.808	0.000	0.000	0.000	0.000	0.808	1.021	0.000
212	6	185	187	213	215	0	1	0.807	0.807	0.807	0.808	0.000	3.229	0.000	0.000
213	6	210	212	214	216	0	1	0.807	0.807	0.807	0.807	0.000	3.227	0.000	0.000
214	6	139	143	209	213	0	1	0.807	0.807	0.807	0.807	0.000	3.229	0.000	0.000
215	6	212	0	0	0	0	1	0.808	0.000	0.000	0.000	0.000	0.808	1.021	0.000
216	6	115	135	177	213	0	1	0.806	0.807	0.806	0.807	0.000	3.227	0.000	0.000

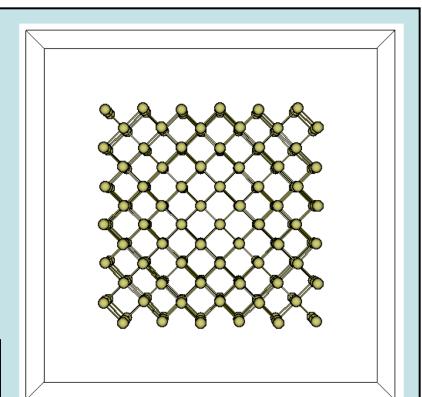
Atom type

Mol#

fort.7

Sum  
BO's

Charge

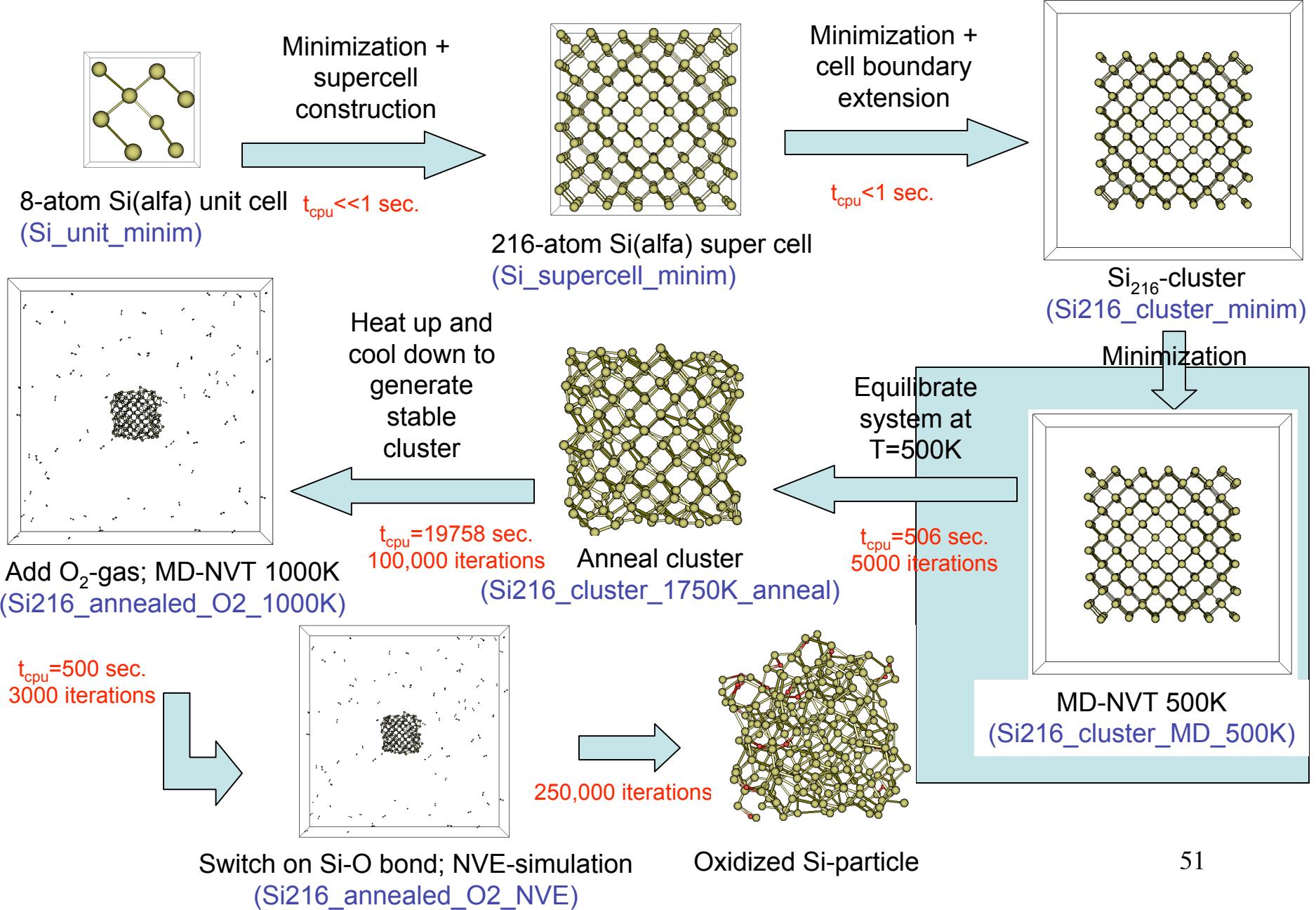


Si<sub>216</sub>-cluster  
(Si216\_cluster\_minim)

Minimization

- Connection table (fort.7) shows that final structure still contains highly undercoordinated atoms (e.g. 209, 211 and 215)
- Energy minimization only yields a local minimum structure

# MD-NVT at T=500K on Si<sub>216</sub>-cluster



# Input files

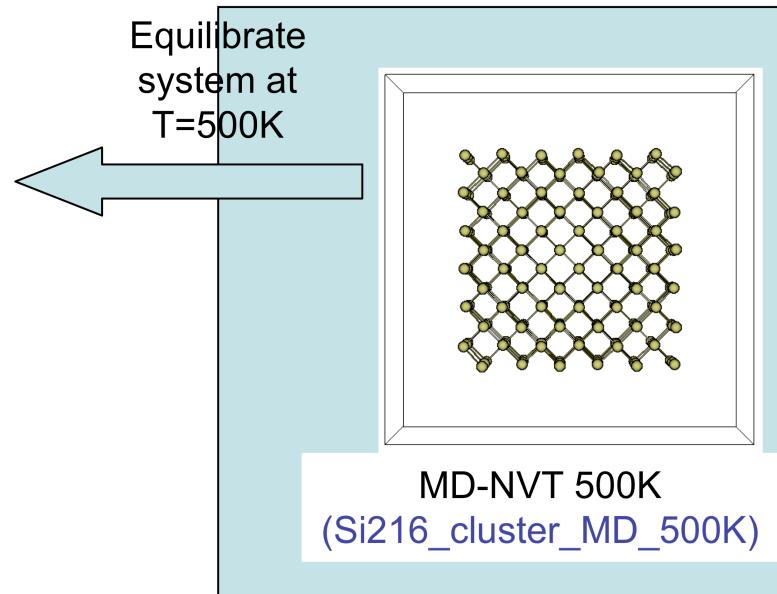
```
...  
0 imetho 0: Normal MD-run 1: Energy minimisation  
1 igeifo 0:xyz-input geometry 1: Biograf input geometry 2: xmol-input...  
80.000 axis1 a (for non-periodical systems)  
80.000 axis2 b (for non-periodical systems)  
80.000 axis3 c (for non-periodical systems)  
0.0050 cutoff2 BO-cutoff for valency angles and torsion angles (do not change)  
0.300 cutoff3 BO-cutoff for bond order for graphs  
4 icharg Charges. 1:EEM 2:- 3: Shielded EEM (default for crystals) 4:...  
1 ichaen Charges. 1:include charge energy 0: Do not include charge energy  
...  
...
```

# MD-parameters

<b>Relevant keyword</b>	<b>Default keyword</b>
1 <b>imdmet</b>	MD-method. 1:NVT 2:Do no use;3 NVE
0.250 <b>tstep</b>	MD-time step (fs)
0500.00 <b>mdtemp</b>	1st MD-temperature
2 itdmet	0: T-damp atoms 1: Energy cons 2:System 3: Mols 4: Anders...
100.0 <b>tdamp1</b>	1st Berendsen/Anderson temperature damping constant (fs)
00000.00 <b>mdpres</b>	MD-pressure (MPa)
00100.0 <b>pdamp1</b>	Berendsen pressure damping constant (fs)
0 inpt	0: Change all cell parameters in NPT-run 1: fixed x 2: fixed y 3:
0005000 <b>nmdit</b>	Number of MD-iterations
00001 <b>ichupd</b>	Charge update frequency
005 <b>iout1</b>	Output to unit 71 and unit 73
0050 <b>iout2</b>	Save coordinates
0 ivels	1:Set vels and accels from moldyn.vel to zero
00025 <b>itrafr</b>	Frequency of trarot-calls
1 iout3	0: create moldyn.xxxx-files 1: do not create moldyn.xxxx-files
1 <b>iravel</b>	1: Random initial velocities
001000 <b>iout6</b>	Save velocity file
000025 <b>irten</b>	Frequency of removal of rotational and translational energy
0 npreit	Nr. of iterations in previous runs
# MM-parameters	

control

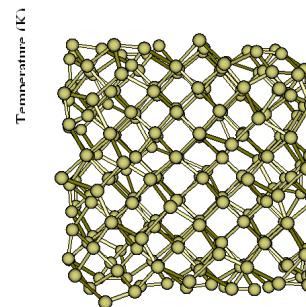
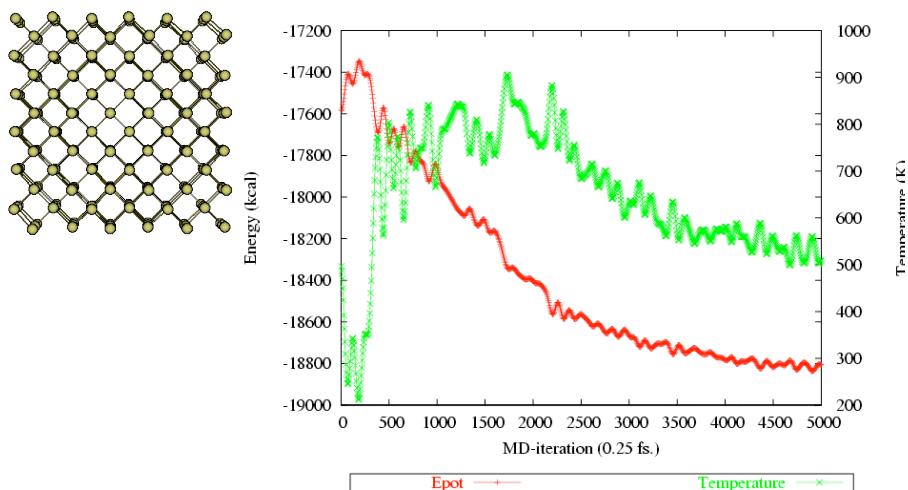
- Other input files :  
**geo,exe,ffield**  
**(standard)**



# Output files

Iter.	Nmol	Epot	Ekin	Etot	T(K)	Eaver(block)	Eaver(total)	Taver	Tmax	Pres(GPa)	sdev(Ep)	sdev(Ear)	Ts	Timestep	RMSG	Totaltime	
5	1	1	-17582.72	319.75	-17262.97	496.62	-17583.95	-17583.95	498.52	499.87	0.00	0.85	0.35	500.00	0.25	1.18	1.25
10	1	1	-17576.16	313.27	-17262.88	486.55	-17579.12	-17581.54	491.10	495.13	0.00	2.22	1.13	500.00	0.25	2.33	2.50
15	1	1	-17565.60	302.89	-17262.71	470.43	-17570.13	-17577.74	477.33	483.79	0.00	3.47	2.33	500.00	0.25	3.44	3.75
20	1	1	-17551.58	289.22	-17262.36	449.20	-17557.44	-17572.66	458.05	466.55	0.00	4.54	3.90	500.00	0.25	4.51	5.00
25	1	1	-17534.90	273.06	-17261.84	424.09	-17541.75	-17566.48	434.39	444.44	0.00	5.36	5.82	500.00	0.25	5.51	6.25
30	1	1	-17516.39	252.04	-17264.35	391.46	-17523.90	-17559.38	402.60	413.61	0.00	5.90	8.03	500.00	0.25	6.41	7.50
35	1	1	-17497.05	233.71	-17263.33	362.99	-17504.81	-17551.59	374.39	385.79	0.00	6.14	10.47	500.00	0.25	7.23	8.75
40	1	1	-17477.84	215.74	-17262.10	335.07	-17485.47	-17543.32	346.14	357.31	0.00	6.06	13.08	500.00	0.25	7.93	10.00
...																	
...																	
4995	1	1	-18806.56	327.09	-18479.47	508.01	-18805.95	-18383.50	507.11	508.01	0.00	0.48	298.85	500.00	0.25	12.31	1248.75
5000	1	1	-18808.19	328.64	-18479.55	510.43	-18807.53	-18383.93	509.45	510.43	0.00	0.52	298.98	500.00	0.25	12.24	1250.00

fort.71

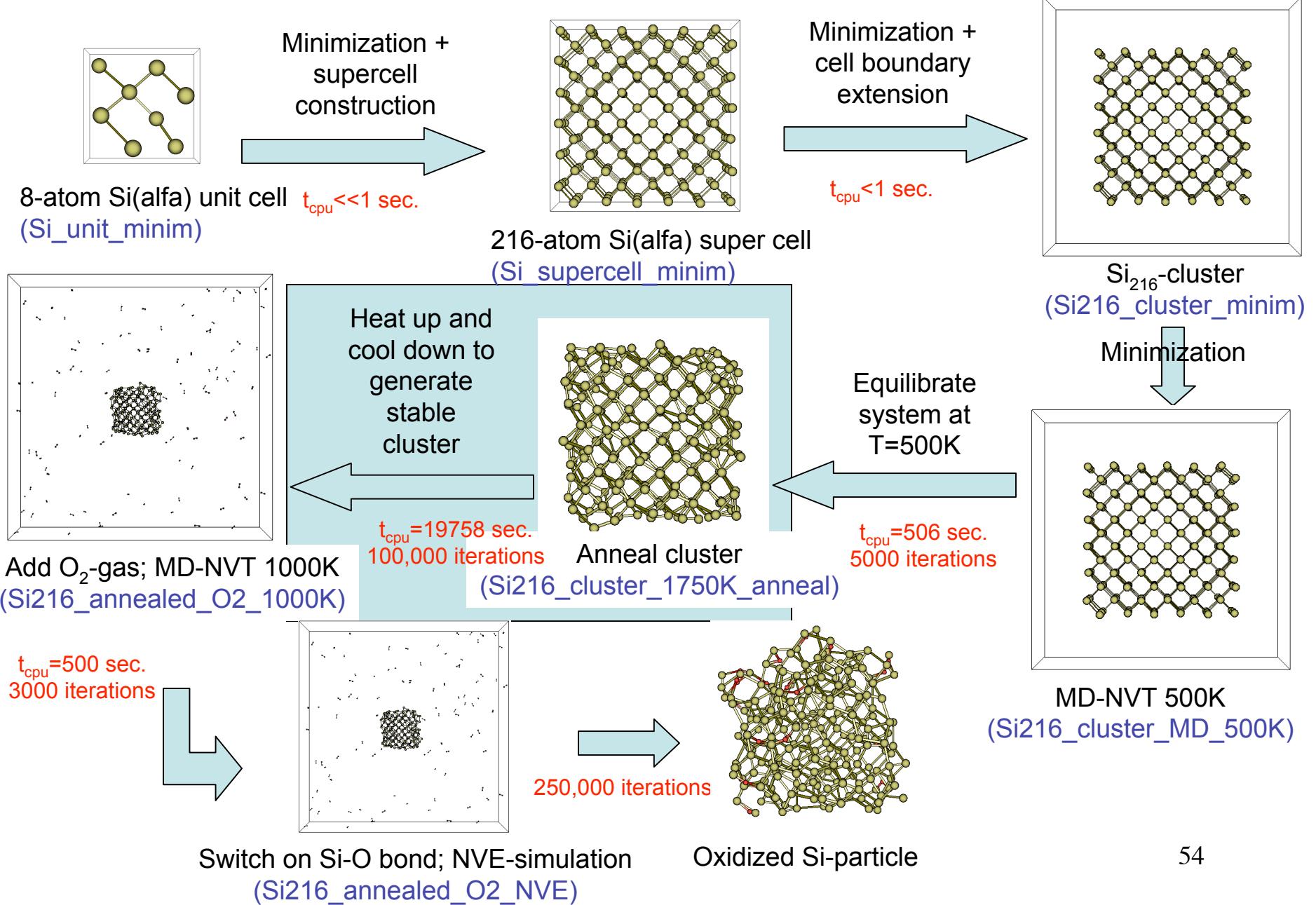


- Potential energy drops as undercoordinated atoms pair up
- Temperature increases due to energy release; thermostat drives temperature back to 500K after locally stable structure is found
- Need to melt the surface to find a more stable structure

## Other output files:

- fort.73: partial energies during MD
- xmolout: .xyz-coordinates
- summary.txt: summary simulation
- molsav.####: restart files
- moldyn.vel: latest restart file

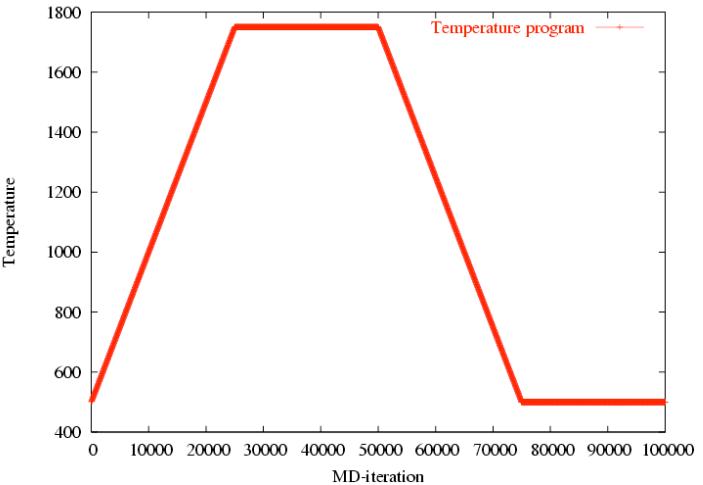
# MD-anneal simulation on Si<sub>216</sub>-cluster



# Input files

- Heat up system until surface melts (1750K)
- Allow surface to rearrange; cool back down to 500K

```
#Temperature regimes
#start #T at1 at2 T1      Tdamp1  dT1
0        1  216  500.0    100.0   0.05
25000   1  216  1750.0   100.0   0.00
50000   1  216  1750.0   100.0  -0.05
75000   1  216  500.0    100.0   0.00
```

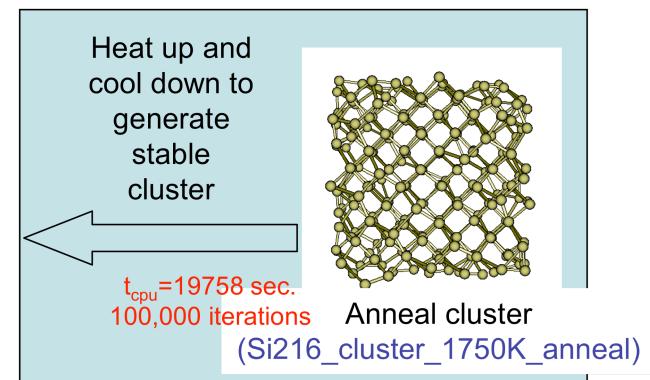


- Temperature program
- Can also define multiple temperature zones (see manual)

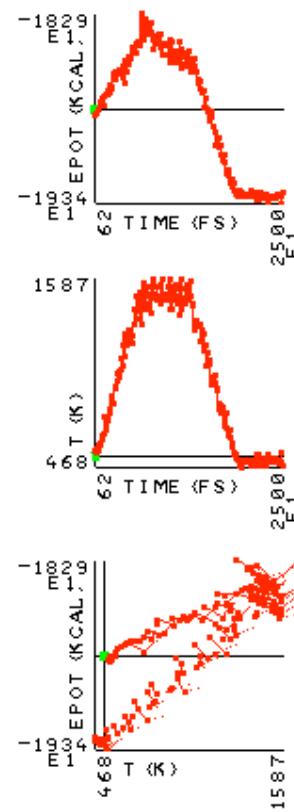
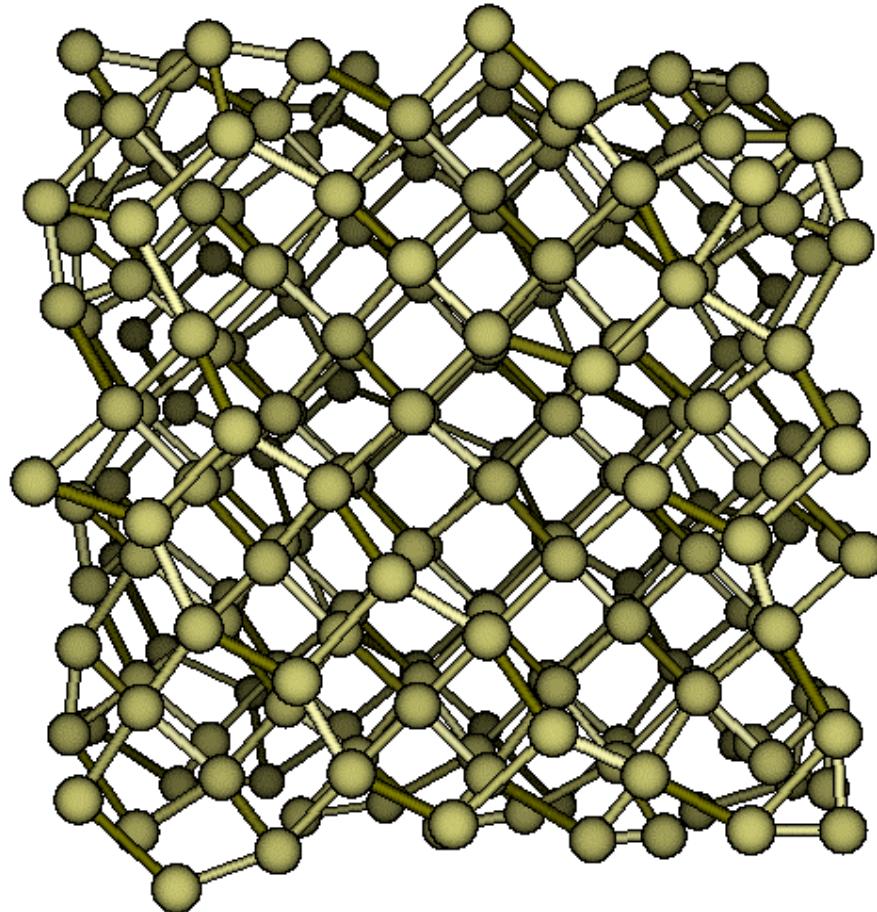
```
Lattice parameters:
80.00000000 80.00000000 80.00000000
90.00000000 90.00000000 90.00000000
216 Atom coordinates (Angstrom):
0.339673667443381E+02 0.365637059552700E+02 0.368293033633050E+02 Si
0.348759012060627E+02 0.359443895605102E+02 0.328454728971770E+02 Si
0.366888761379082E+02 0.368854824846820E+02 0.340052086818958E+02 Si
0.357873541349899E+02 0.329489764194424E+02 0.348457757706991E+02 Si
0.339784717276348E+02 0.341471609565867E+02 0.340464490715064E+02 Si
...
...
...
```

vels (moldyn.vel from  
500K-equilibration)

- Contains cell parameters, positions, velocities, accelerations
- Overrides the geo-file (beware!)
- Hierarchy: vels overrides geo, geo overrides control



# Output files

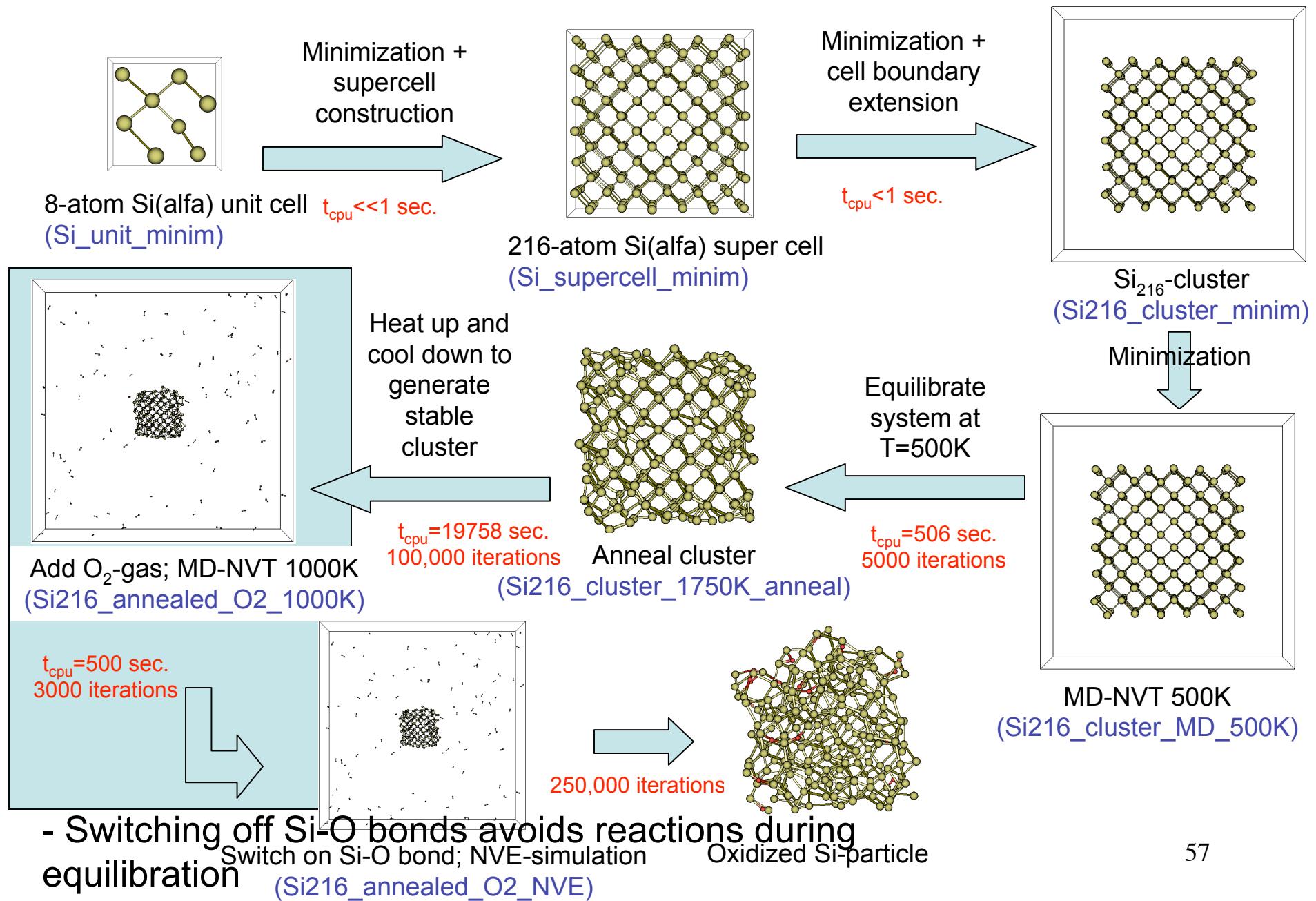


Relevant output files :

- fort.75 (expanded temperature information)
- summary.txt
- xmolout
- fort.71
- fort.73
- fort.7

- SI 216 MD ANNEAL
- Surface melts, leading to major rearrangement of surface atoms
  - Final structure is substantially more stable than initial 500K-structure
  - Multiple anneal-simulations may be required to find final cluster structure

Add 100 O<sub>2</sub>-molecules; equilibrate at T=1000K; switch off Si-O bonds



# Input files

```
XTLGRF 200
DESCRP 100_O2_Si216
REMARK .bgf-file generated by xtob-script
CRYSTX 80.00000 80.00000 80.00000 90.00000 90.00000 90.00000
HETATM 1 O      28.28830 76.86782 32.07423 O 0 0 2.07483
HETATM 2 O      29.24999 76.94106 31.36024 O 0 0 2.07483
HETATM 3 O      15.28491 27.65341 49.23293 O 0 0 2.07483
HETATM 4 O      15.91362 28.07402 48.30137 O 0 0 2.07483
HETATM 5 O      68.30412 41.99475 55.05177 O 0 0 2.07483
HETATM 6 O      67.85973 42.73083 54.21468 O 0 0 2.07483
...
...
HETATM 413 Si   44.16213 44.57315 44.99264 Si 0 0 2.07483
HETATM 414 Si   43.11118 46.05790 46.31335 Si 0 0 2.07483
HETATM 415 Si   46.76759 45.42089 47.16145 Si 0 0 2.07483
HETATM 416 Si   43.10233 43.22858 43.57832 Si 0 0 2.07483
END
```

geo

- Other input files : exe, control  
(standard)

```
Reactive MD-force field: Si/SiO/SiN interactions March 9 2006 switched off Si-O
```

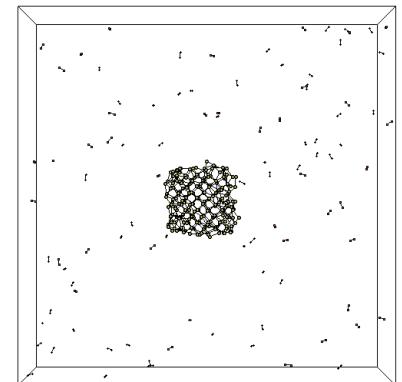
```
...
...
3 6 000.0000 000.0000 0.0000 -0.7316 -0.3000 1.0000 36.0000 0.6482
     8.7560 -0.4622 30.0000 1.0000 -0.0987 7.7664 1.0000 0.0000
4 6 119.7136 41.2405 43.3991 -0.2060 -0.3000 1.0000 36.0000 0.7957
     0.8189 -0.2614 9.4060 1.0000 -0.1245 6.1856 1.0000 0.0000
6 6 78.0276 54.0531 30.0000 0.5398 -0.3000 1.0000 16.0000 0.0476
     0.2865 -0.8055 7.1248 1.0000 -0.0681 8.6957 0.0000 0.0000
```

Modified force field parameter

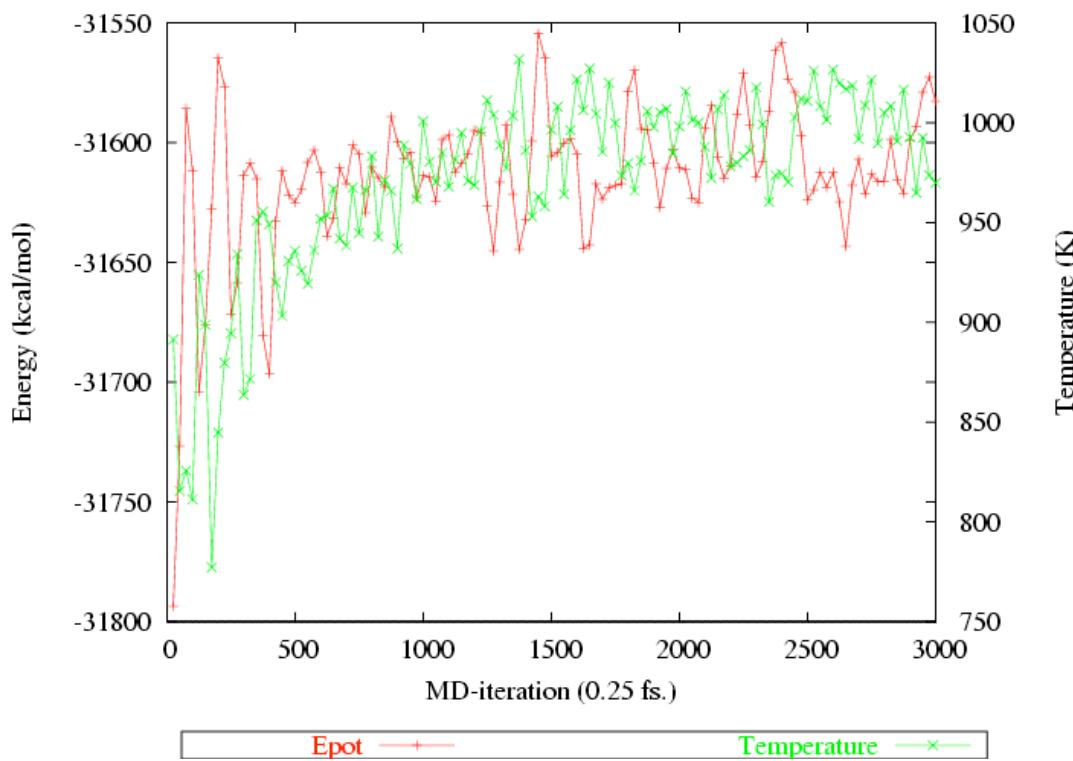
Default parameter

ffield

- Switching off Si-O bonds avoids reactions during equilibration



# Output files



Relevant output files :

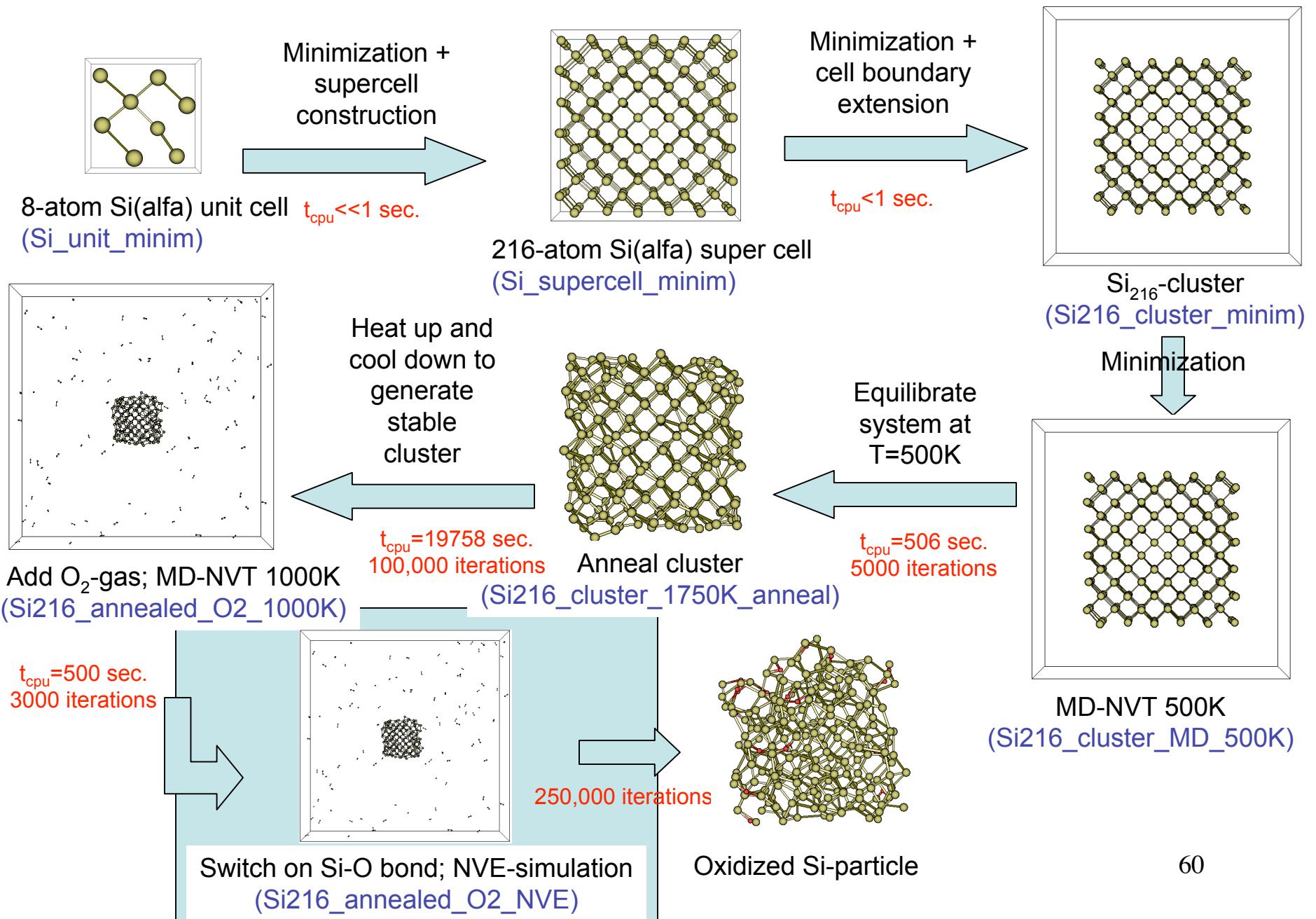
- fort.71
- summary.txt
- xmolout
- fort.71
- fort.73
- fort.7
- moldyn.vel

Bond order cutoff:0.3000		
Iteration Freq.	Molecular formula	Molecular mass
0	100 x O <sub>2</sub>	31.9980
0	1 x Si216	6060.9600
...		
...		
Iteration Freq.	Molecular formula	Molecular mass
3000	100 x O <sub>2</sub>	31.9980
3000	1 x Si216	6060.9600
Total number of molecules:	101	
Total number of atoms:	416	
Total system mass:	9260.76	

molfra.out

- molfra.out-file indicates no reactions have occurred
- System is equilibrated at 1000K; now switch Si-O bonds back on and use moldyn.vel to start NVE-simulation

# NVE-simulation on $\text{Si}_{216}$ -particle/ $\text{O}_2$ starting at T=1000K

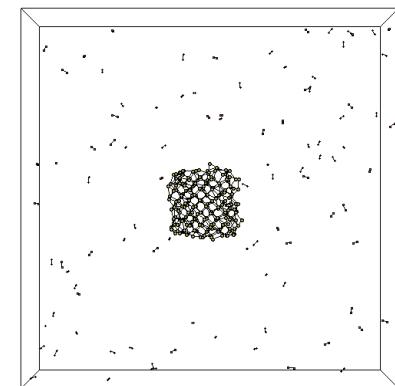


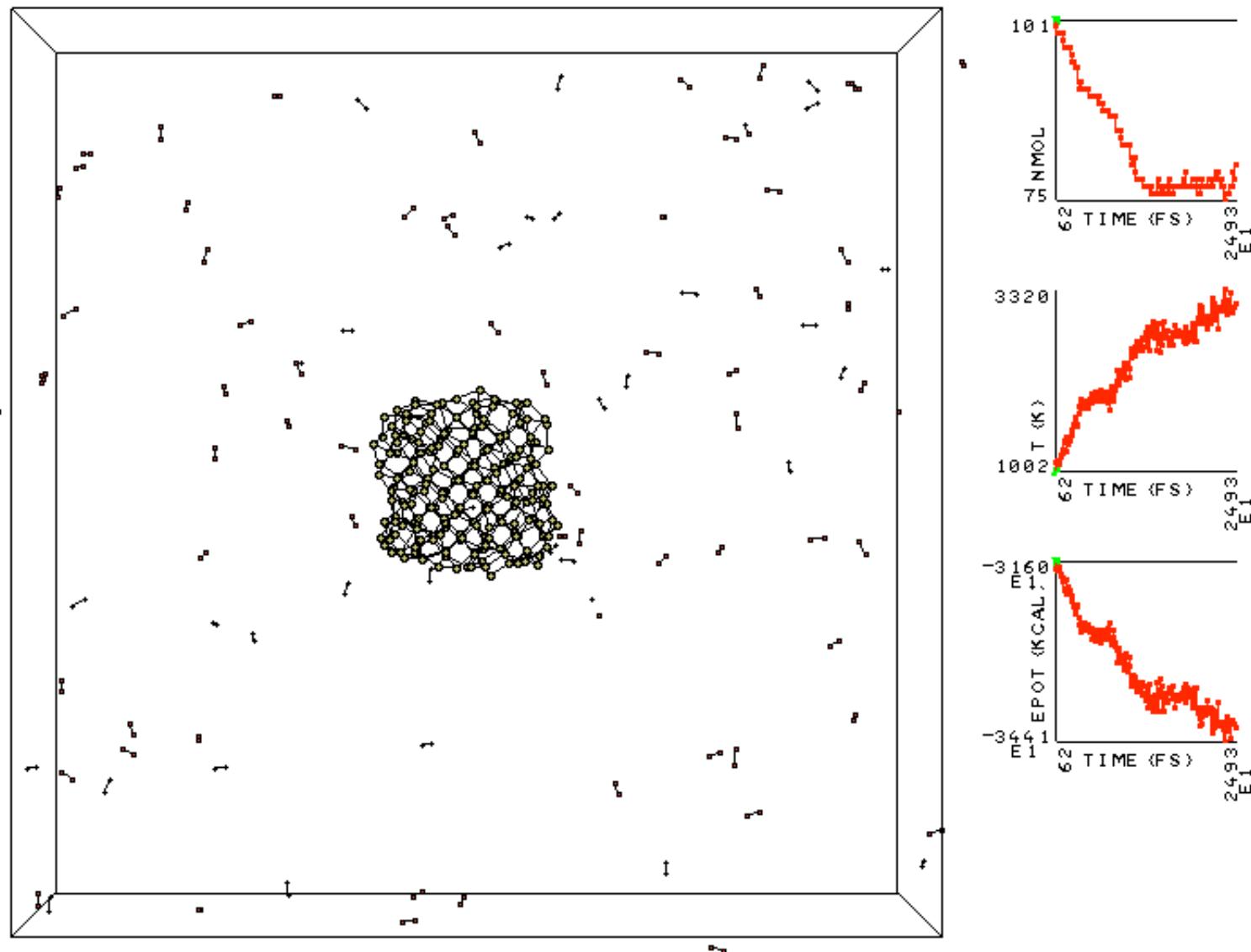
# Input files

```
...  
0 imetho 0: Normal MD-run 1: Energy minimisation  
1 igeofo 0:xyz-input geometry 1: Biograf input geometry 2: xmol-input...  
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 cutoff2 BO-cutoff for valency angles and torsion angles (do not change)  
0.300 cutoff3 BO-cutoff for bond order for graphs  
4 icharg Charges. 1:EEM 2:- 3: Shielded EEM (default for crystals) 4:...  
1 ichaen Charges. 1:include charge energy 0: Do not include charge energy  
...  
...  
# MD-parameters  
3 imdmet MD-method. 1:NVT 2:Do no use;3 NVE  
0.250 tstep MD-time step (fs)  
0500.00 mdtemp 1st MD-temperature  
2 itdmet 0: T-damp atoms 1: Energy cons 2:System 3: Mols 4: Anders...  
100.0 tdamp1 1st Berendsen/Anderson temperature damping constant (fs)  
0000.00 mdpres MD-pressure (MPa)  
00100.0 pdamp1 Berendsen pressure damping constant (fs)  
0 inpt 0: Change all cell parameters in NPT-run 1: fixed x 2: fixed y 3:  
0250000 nmdit Number of MD-iterations  
00001 ichupd Charge update frequency  
025 iout1 Output to unit 71 and unit 73  
0250 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  
010000 iout6 Save velocity file  
000025 irten Frequency of removal of rotational and translational energy  
0 npreit Nr. of iterations in previous runs  
# MM-parameters
```

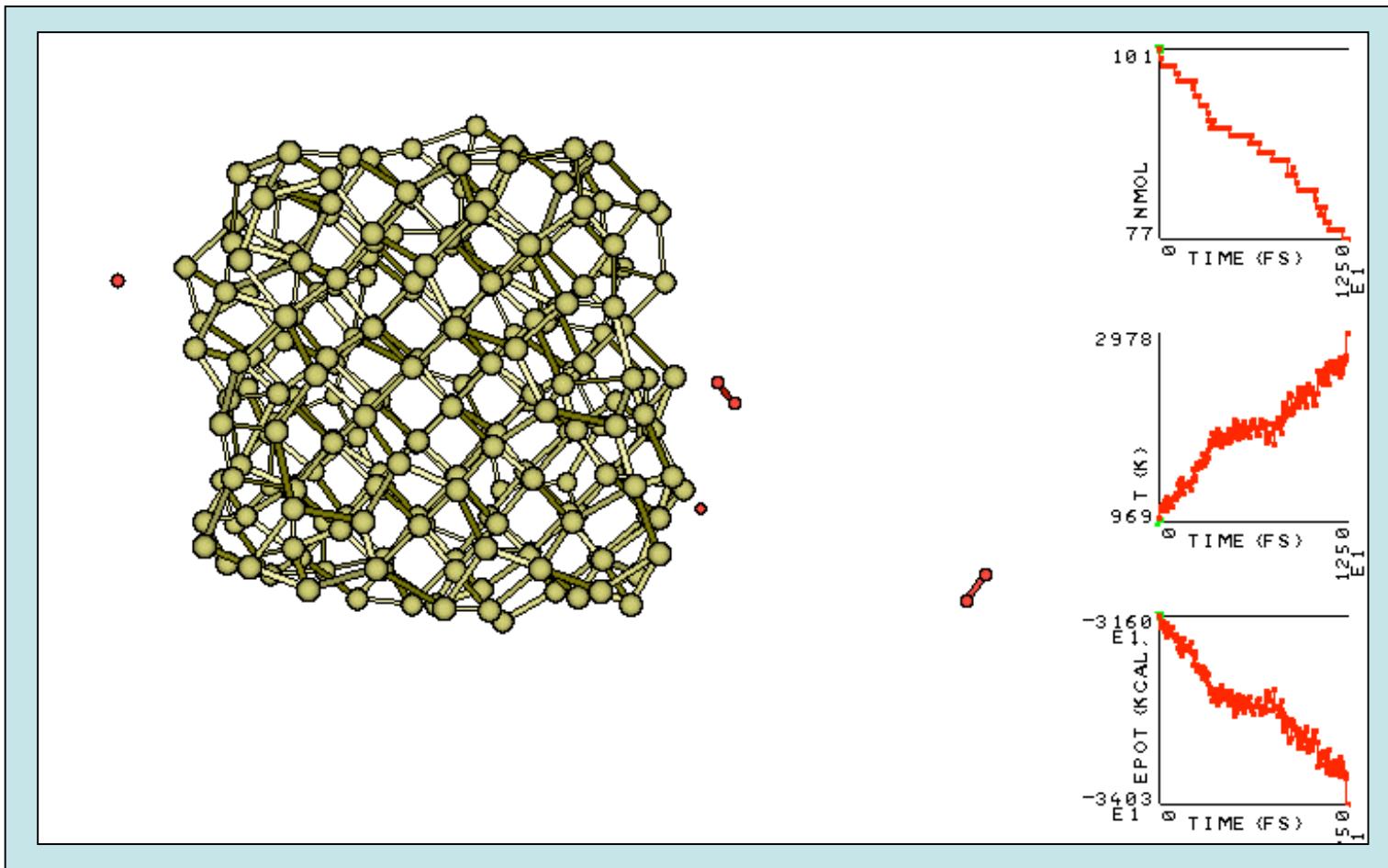
control

- Copied moldyn.vel from 1000K-equilibration to vels
- Other input files : exe, geo, ffield (standard)

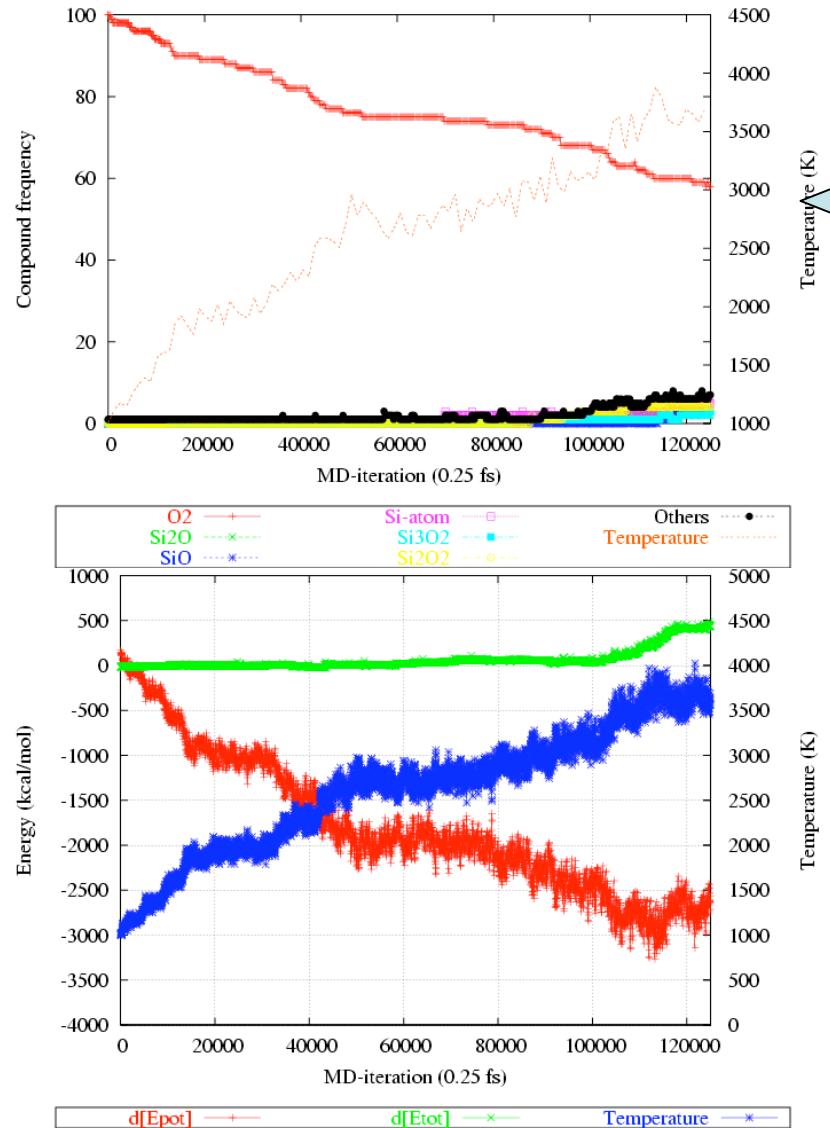




- Highly exothermic reaction
- Temperature rises to >3000K; particle becomes unstable



# Output files



Bond order cutoff:0.3000

Iteration Freq. Molecular formula Molecular mass

0	100 x O <sub>2</sub>	31.9980
0	1 x Si <sub>216</sub>	6060.9600
...	...	...
125000	1 x O <sub>52</sub> Si <sub>181</sub>	5910.8080
125000	1 x O <sub>3</sub> Si <sub>3</sub>	132.1770
125000	58 x O <sub>2</sub>	31.9980
125000	3 x O <sub>2</sub> Si <sub>3</sub>	116.1780
125000	3 x OSi	44.0590
125000	4 x O <sub>2</sub> Si <sub>2</sub>	88.1180
125000	1 x O <sub>2</sub> Si	60.0580
125000	2 x OSi <sub>2</sub>	72.1190
125000	2 x O	15.9990
125000	1 x O <sub>3</sub> Si <sub>2</sub>	104.1170
125000	1 x O <sub>3</sub>	47.9970
125000	5 x Si	28.0600

Total number of molecules: 82  
 Total number of atoms: 416  
 Total system mass: 9260.76

**molfra.out**

Other relevant output files :

- fort.71
- summary.txt
- xmolout
- fort.71
- fort.73
- fort.7
- moldyn.vel

- Energy is reasonably well-conserved until iteration 100,000
- Better energy conservation can be obtained by reducing the time-step at high temperatures

# Additional ReaxFF features

## Multiple thermostats

tregime.in

### #Temperature regimes

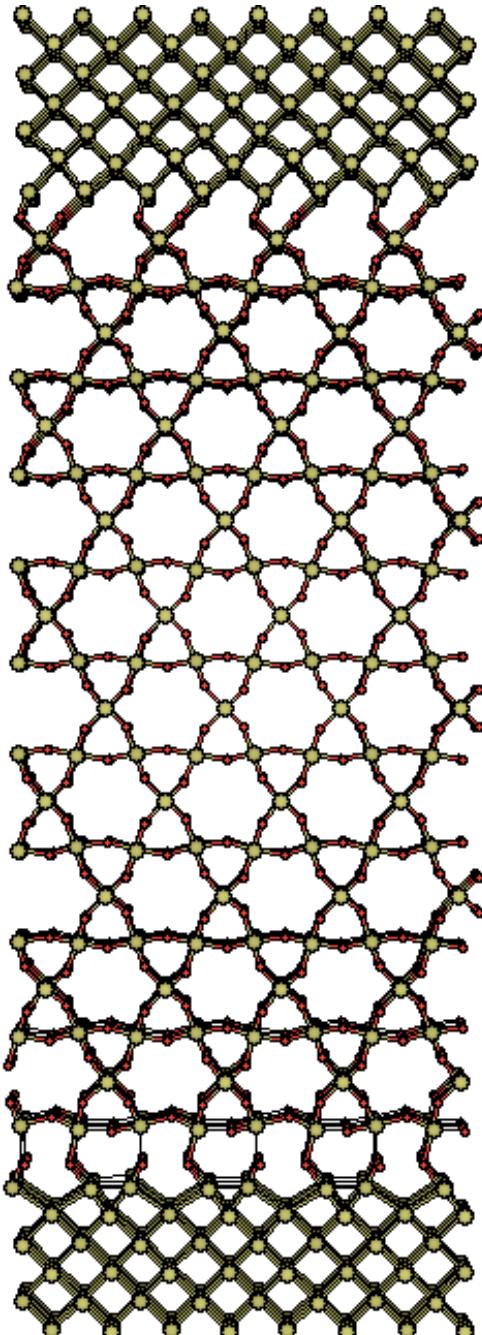
#start	#T	at1	at2	T1	Tdam1	dT1	at3	at4	T2	Tdam2	dT2
0	2	1	152	200.0	50.0	0.29	153	256	100.0	2.5	0.00
20000	2	1	152	6000.0	50.0	-0.29	153	256	100.0	2.5	0.00
40000	2	1	152	200.0	50.0	0.00	153	256	100.0	2.5	0.00

Nr. of  
temperature  
zones in program

Start iteration of  
temperature  
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

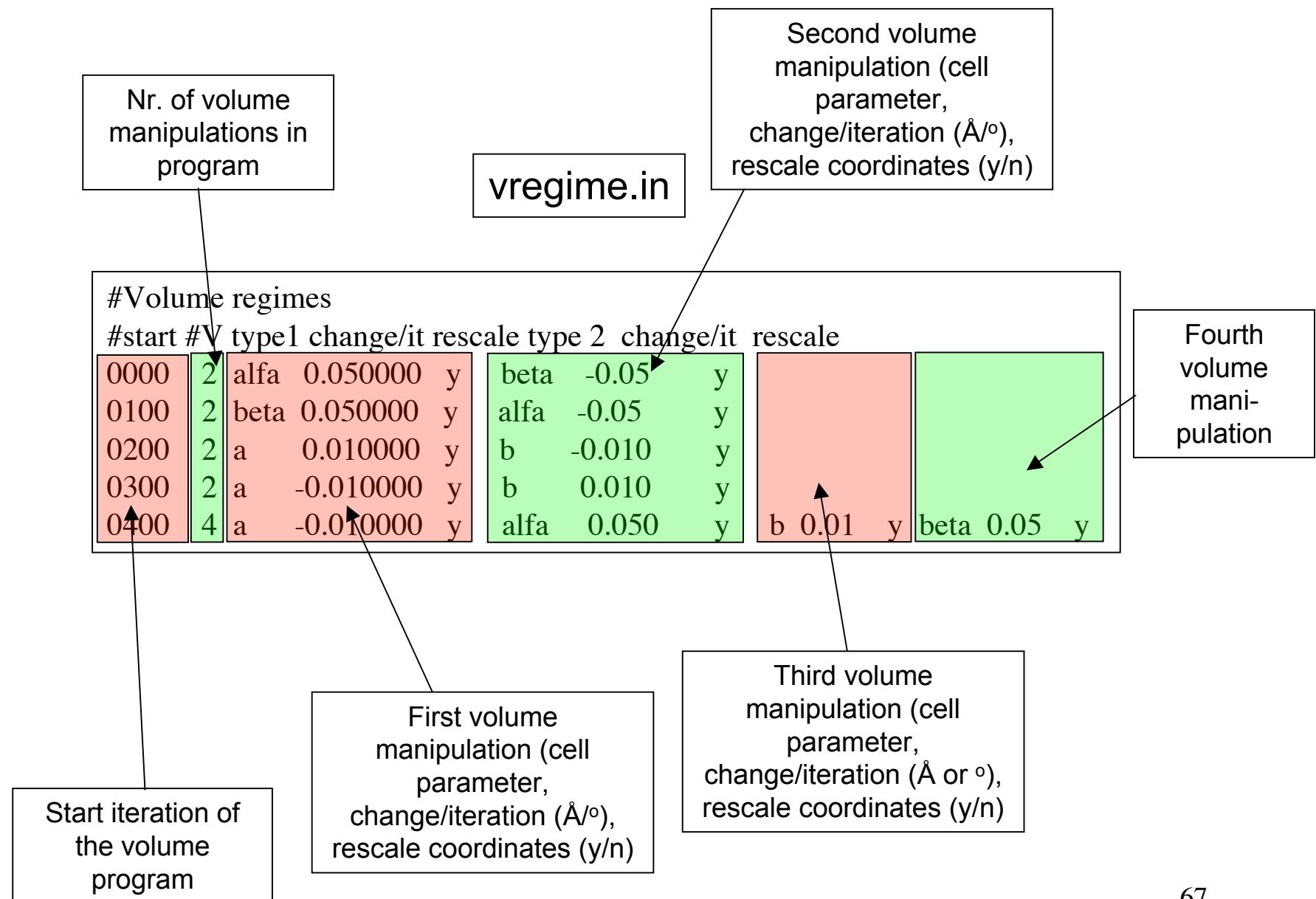
Example: Si/SiO<sub>2</sub> interface

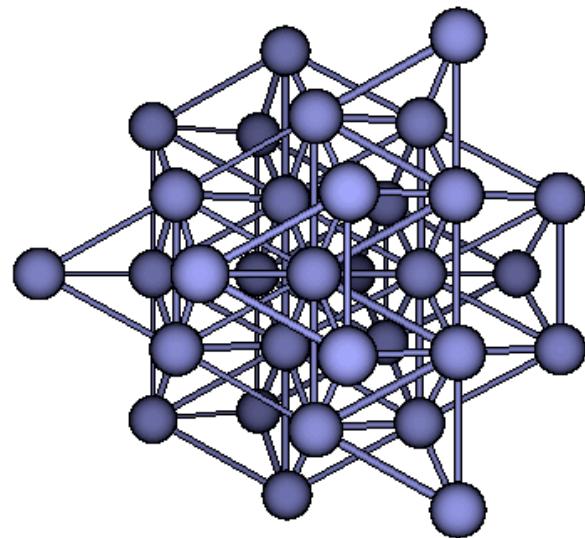
To generate an amorphous SiO<sub>2</sub>/Si(alpha) 2 temperature zones are defined:

- 1) Si-phase: keep at 100K
- 2) SiO<sub>2</sub>-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
```

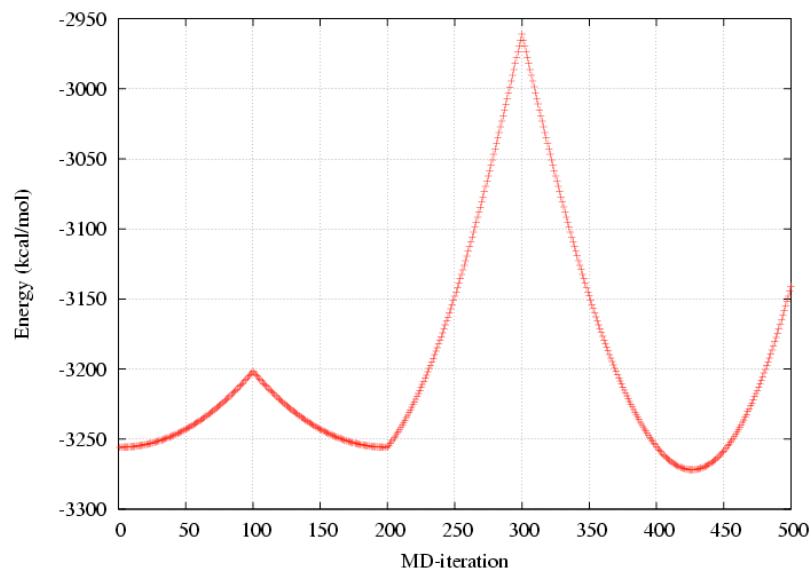
## Cell volume manipulation





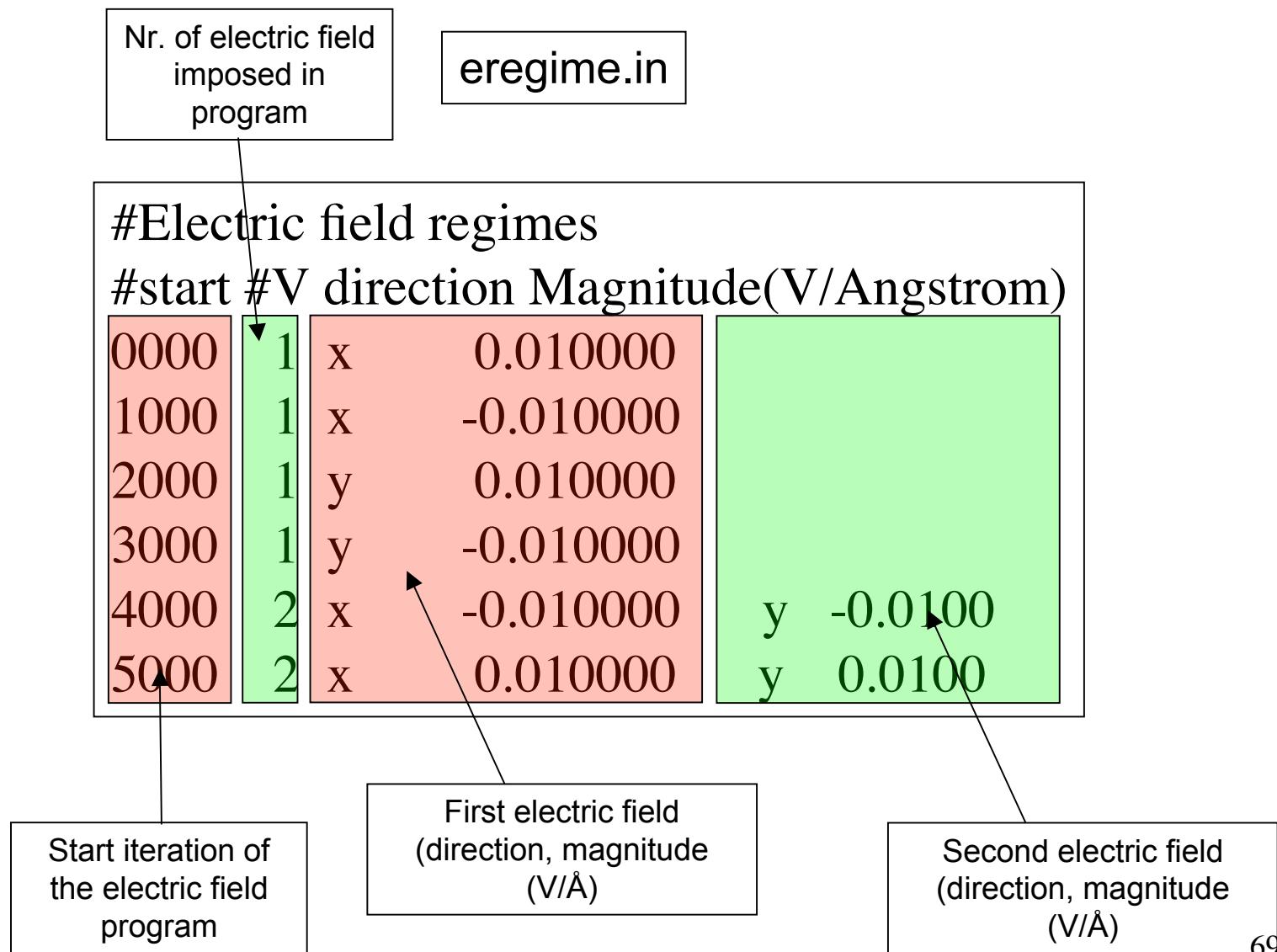
## Example: 32 atom Co-fcc supercell

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

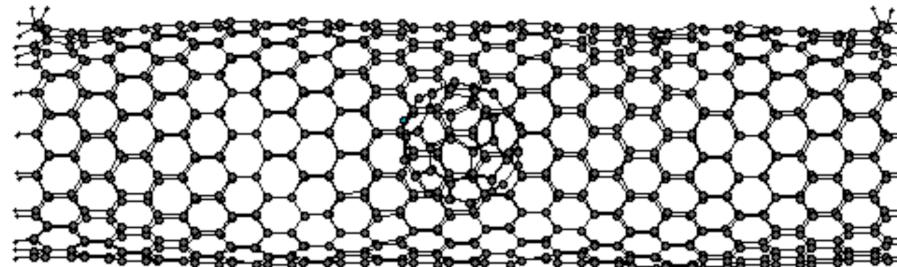


```
#Volume regimes
#start #V type1 change/it rescale type 2 change/it rescale
0000 2 alfa 0.050000 y beta -0.05 y
0100 2 beta 0.050000 y alfa -0.05 y
0200 2 a 0.010000 y b -0.010 y
0300 2 a -0.010000 y b 0.010 y
0400 4 a -0.010000 y alfa 0.050 y b 0.01 y beta 0.05 y
```

## Electric field manipulation



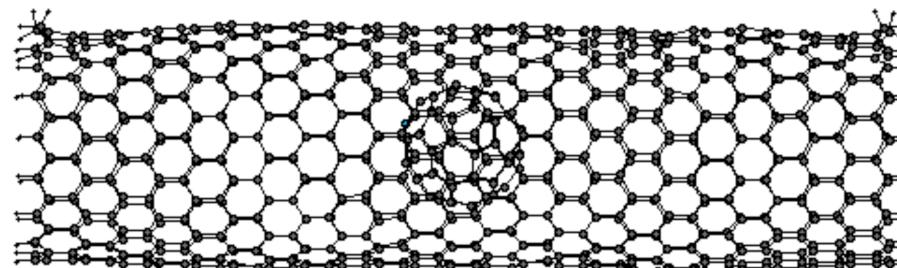
+



Weak electric field

NC<sub>59</sub>-buckyball in H-terminated nanotube

-



Strong electric field

- electric field is included in EEM-equations and can polarize charges

## Distance, angle and torsion restraints

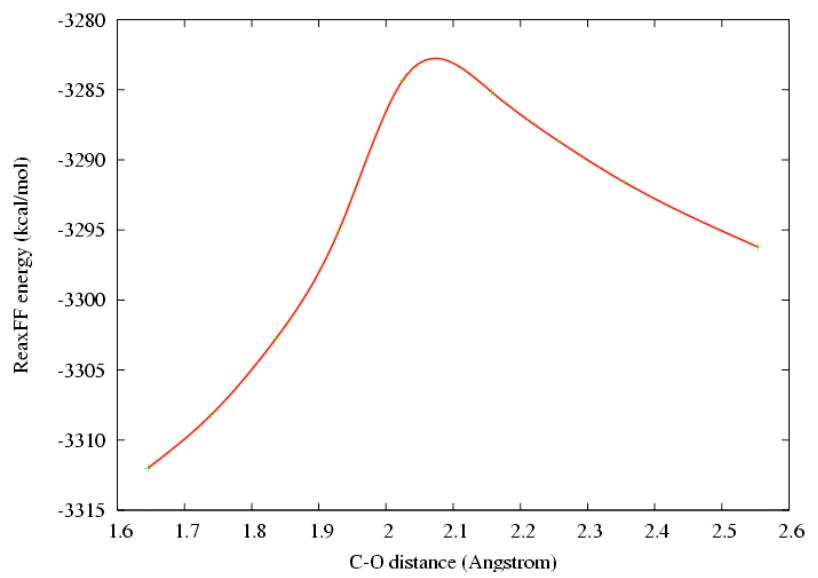
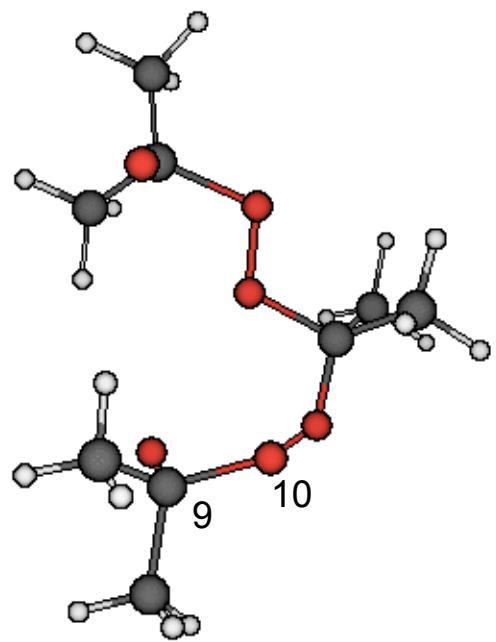
### geo-file with permanent, non-sliding bond restraint

```
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,  $R_{ij}$ ,  $p_{res1}$ ,  
 $p_{res2}$ )

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

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

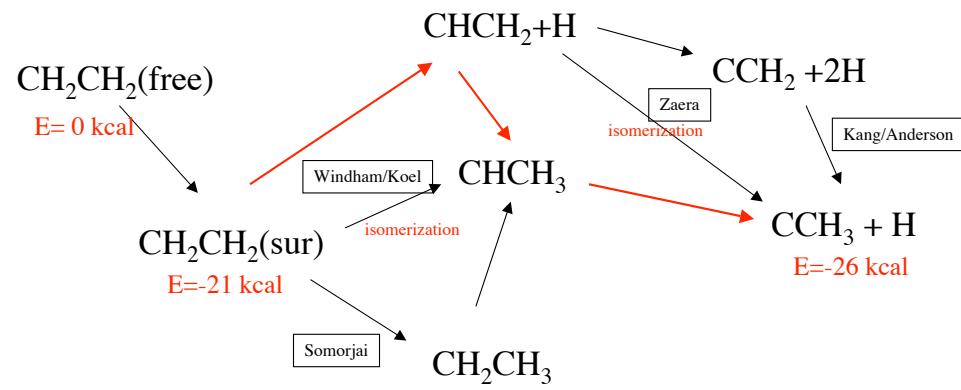
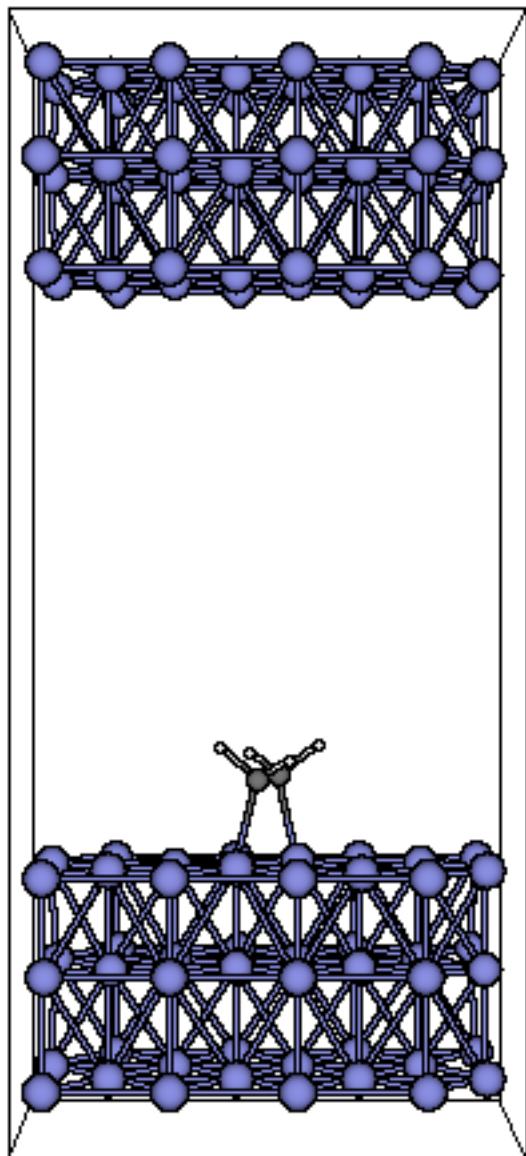


## geo-file with programmed sliding restraints

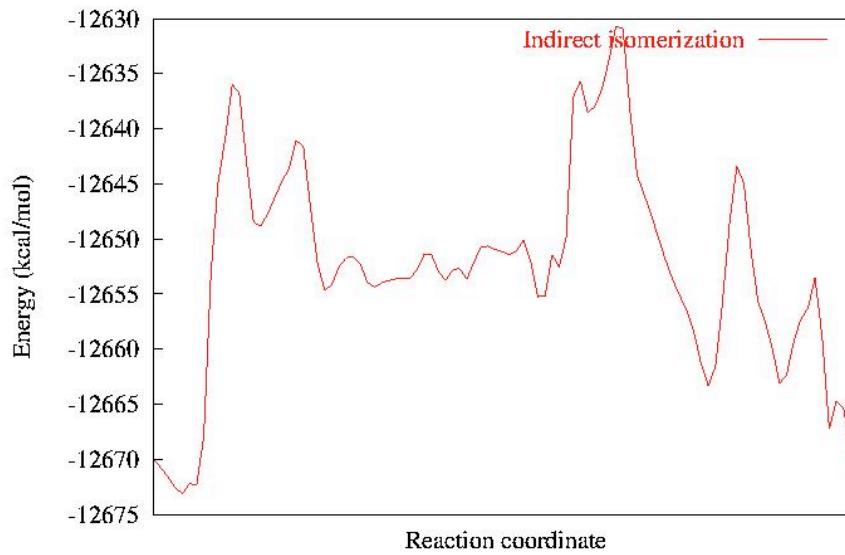
XTLGRF 200						
DESCRP Ethene_Pt_1						
RUTYPE NORMAL RUN						
#	At1	At2	R12	Force1	Force2	dR12/dIter(MD) Start (MD) End (MD)
BOND RESTRAINT	3	38	3.1000	1000.00	1.0000	-0.0003200 0 5000
BOND RESTRAINT	2	3	1.1000	1000.00	1.0000	0.0005000 3000 5000
BOND RESTRAINT	2	3	2.1000	0000.00	1.0000	0.0002500 5000 10000
BOND RESTRAINT	3	38	1.5000	0250.00	1.0000	0.0004000 7500 10000
BOND RESTRAINT	3	16	3.1000	1000.00	1.0000	-0.0003200 5000 10000
BOND RESTRAINT	3	16	1.5000	0250.00	0.2500	0.0004000 12500 15000
BOND RESTRAINT	3	17	3.7000	1000.00	1.0000	-0.0004400 10000 15000
BOND RESTRAINT	3	26	3.9000	1000.00	1.0000	-0.0004600 15000 20000
BOND RESTRAINT	1	3	3.0000	1000.00	1.0000	-0.0003800 20000 25000
BOND RESTRAINT	17	3	2.0000	0250.00	0.2500	0.0002000 20000 25000
BOND RESTRAINT	26	3	2.0000	0250.00	0.2500	0.0002000 20000 25000
BOND RESTRAINT	1	31	2.5000	1000.00	1.0000	0.0015000 25000 26000
BOND RESTRAINT	2	4	1.1000	0250.00	1.0000	0.0003500 26000 28500
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	5.32771	16.43303	6.19999	C 1 1 0.00000
HETATM	2	C	5.70462	16.41203	4.79278	C 1 1 0.00000
HETATM	3	H	4.98171	15.85375	4.18962	H 1 1 0.00000
HETATM	4	H	6.51890	15.68332	4.61650	H 1 1 0.00000
HETATM	5	H	4.60169	15.63429	6.40317	H 1 1 0.00000
HETATM	6	H	6.16647	16.03195	6.81934	H 1 1 0.00000
.....						
.....						
END						

- Only available for MD-simulation

## ReaxFF MD-simulation using sliding bond restraints to drive reactions



Ethylene  $\rightarrow$  CHCH<sub>3</sub> conversion on Pt(111)surface  
ReaxFF minimization with restraints to drive reaction



# Force field optimization

## trainset.in-file: defines ReaxFF training set

```
CHARGE
#Im-OH complex
zwitter6 0.05 19 -0.02294
ENDCHARGE
CELL PARAMETERS
chex_cryst 0.40 c 16.40
ENDCELL PARAMETERS
FREQUENCIES
cyclohexane_vib 50.00 50.00 cyclohexane.out
ENDFREQUENCIES
HEATFO
methane 2.00 -17.80
ENDHEATFO
GEOMETRY
h2co_min 0.02 1 2      1.207
h2co_min 2.00 2 1 3    122.4
ENDGEOMETRY
ENERGY
#CN triple bond dissociation
400.0 + hcn_min /1 - cn1 /1          -943.30
100.0 + hcn_min /1 - cn2 /1          -437.00
25.0  + hcn_min /1 - cn3 /1          -175.00
10.0  + hcn_min /1 - cn4 /1          -51.00
5.0   + hcn_min /1 - cn5 /1          -5.40
5.0   + hcn_min /1 - cn6 /1          -2.50
5.0   + hcn_min /1 - cn7 /1          -22.20
10.0  + hcn_min /1 - cn8 /1          -52.70
10.0  + hcn_min /1 - cn9 /1          -87.20
10.0  + hcn_min /1 - cn10 /1         -121.90
10.0  + hcn_min /1 - cn11 /1         -154.80
10.0  + hcn_min /1 - cn12 /1         -184.70
10.0  + hcn_min /1 - cn13 /1         -211.40
10.0  + hcn_min /1 - cn14 /1         -245.60
ENDENERGY
```

## fort.99-file: reports ReaxFF results for the training set

Charge atom:	19		FField	QM/Lit	Weight	Error	Total err
CH2NH_NH3h1		Bond distance: 2 6	0.1107	-0.0229	0.0500	7.1485	7.1485
			2.2044	2.1400	0.0500	1.6577	8.7952
Energy +zwitter1/ 1 -zwitter2/ 1			-5.7560	-4.8200	2.5000	0.1402	8.1971
Energy +zwitter1/ 1 -zwitter3/ 1			-9.6444	-17.2100	2.5000	9.1581	17.3453
Energy +zwitter1/ 1 -zwitter4/ 1			-15.8228	-27.7100	2.5000	22.6091	39.9144
Energy +zwitter1/ 1 -zwitter5/ 1			-26.6593	-34.9300	2.5000	10.9448	41.8589
Energy +zwitter1/ 1 -zwitter6/ 1			-31.2948	-41.1200	2.0000	24.1337	66.0897
Energy +phenol_CH3OHh1/ 1 -phenol_CH3OHh2/ 1			-6.0750	-4.5500	0.5000	9.3025	75.3922