Reactive Force Fields in Particular ReaxFF and Application Possibilities

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Part I: General Concepts and Comparison to other Simulation Methods

Part II: ReaxFF as Reactive Force Field

Part III : Connection to Energy Landscapes – not included

Notice

The material presented in Part I and II is mainly based on the following presentations:

van Duin, A. C. T. Lecture Notes CH121 CalTech (2008) - *Applications of the ReaxFF reactive force Field and Reactive force fields: concepts of ReaxFF*

van Duin, A. C. T., Chenoweth, K., and Goddard, B. Interatomic Potentials Workshop July 2008, Oxford - *ReaxFF force fields*

van Duin, A. C. T. ARL workshop August 2008. - *Using the ReaxFF program.*

Quenneville, J., *Summer School on Computational Materials Science July 31 - August 11, 2006 · University of Illinois* - *Reactive Empirical Force Fields*

Part I: General Concepts and Comparison to other Simulation Methods

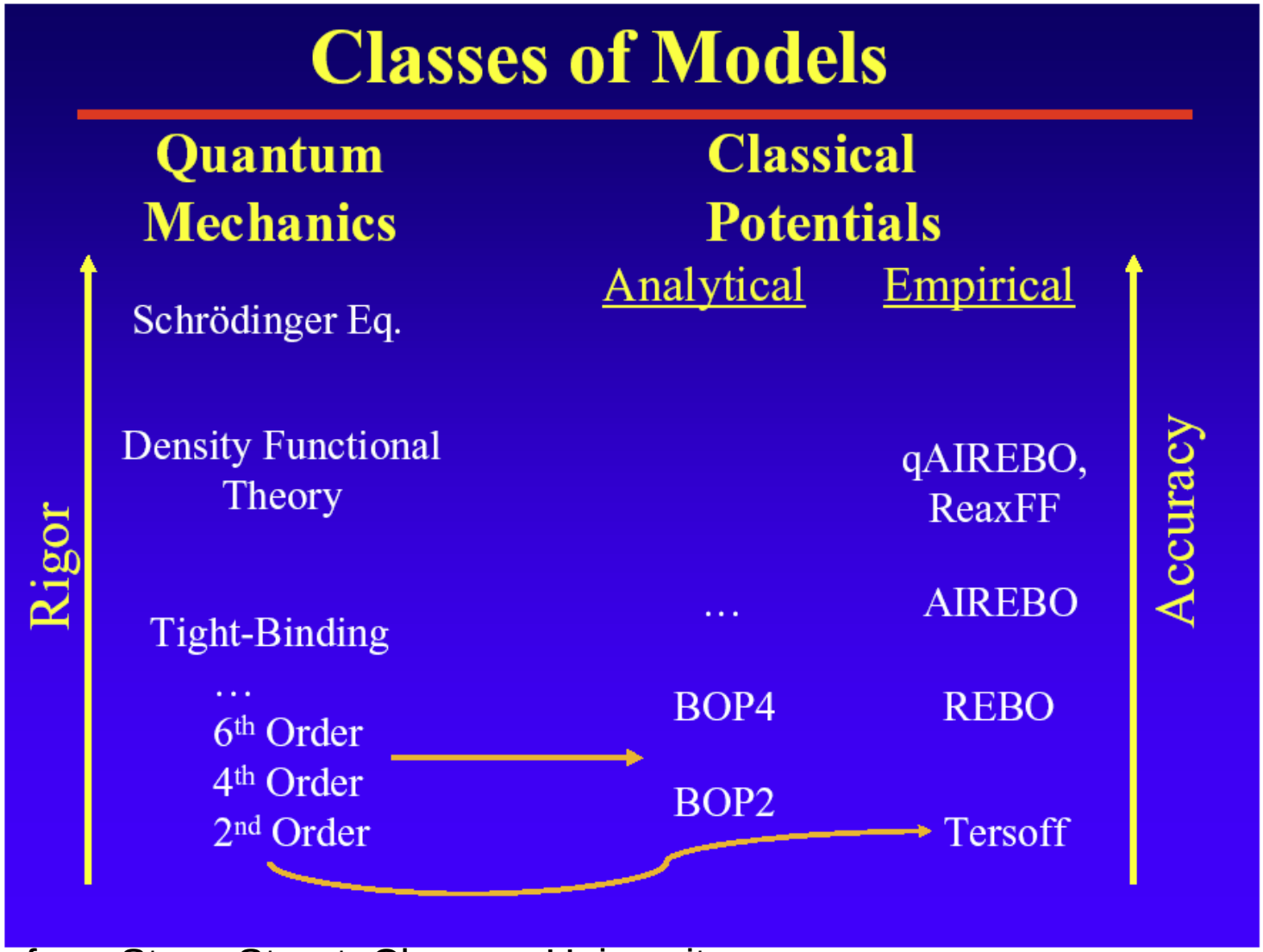
Approaches to reactive MD

I. Computational Expensive QM/MD (e.g. Raty et al., PRL 2005)

II. Semiempirical Methods – speed up QM with empirical assumptions
- CINDO/MINDO/AM1/MOPAC
  (e.g. Pople and Segal, JCP 1966; Stewart, J. Comp. Chem. 1989)
- Tight-binding (e.g. McMahan and Klepeis, PRB 1997)
- Analytical Bond Order Potentials (e.g. Pettifor and Oleinik, PRB 1999)

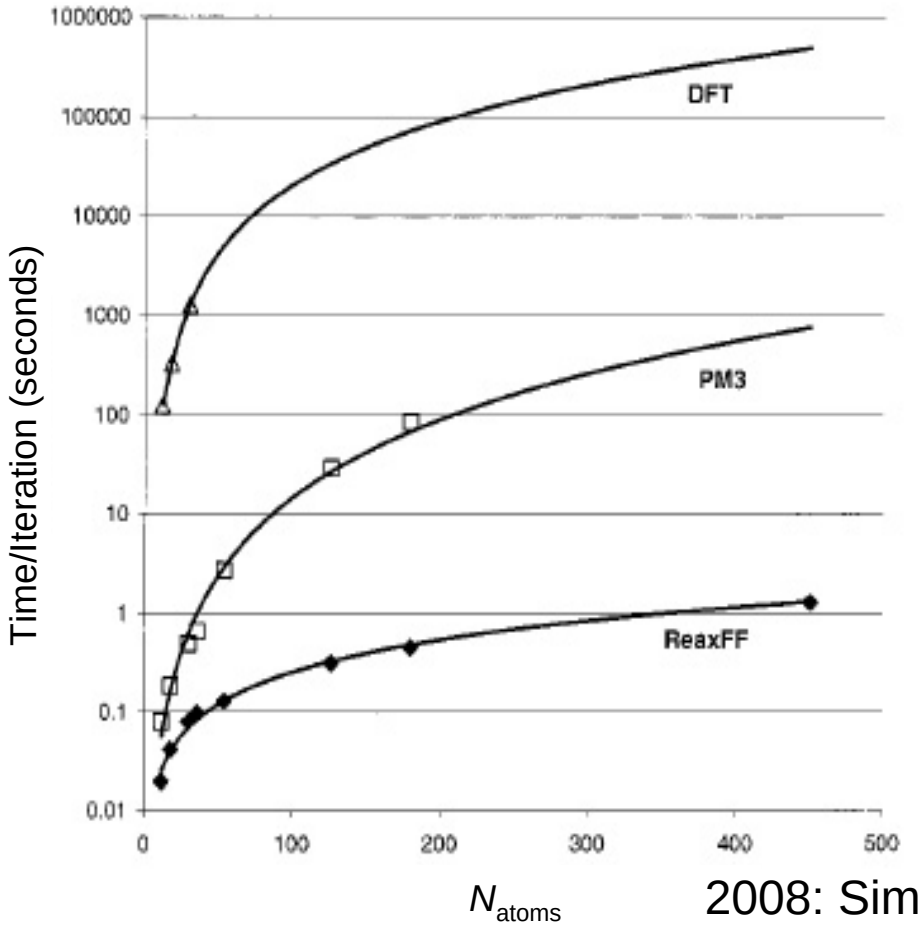
III. Empirical bond-order based force fields – Force Field Methods with ability to simulate reactions
- Tersoff /Brenner /AIREBO (Tersoff, PRL 1988; Brenner, PRB 1990, Stuart et al., JCP 2000)
- LCBOP (de Los et al., PRB 2005)
- EDIP (e.g. Bazant and Kaxiras, PRL 1996)
- ReaxFF (e.g. van Duin et al. JPC-A 2001)

Model Comparison



from Steve Stuart, Clemson University

Benchmark Results



Quenneville, J., (2006).

- ReaxFF is 10-50 times slower than non-reactive force fields (serial, 1 CPU & 4000 Atoms):
[van Duin, A. C. T. , CMDF workshop, August 23 2005, Materials Simulation Center, California Institute of Technology - *ReaxFF reactive force field: A new link from QM to MM*]

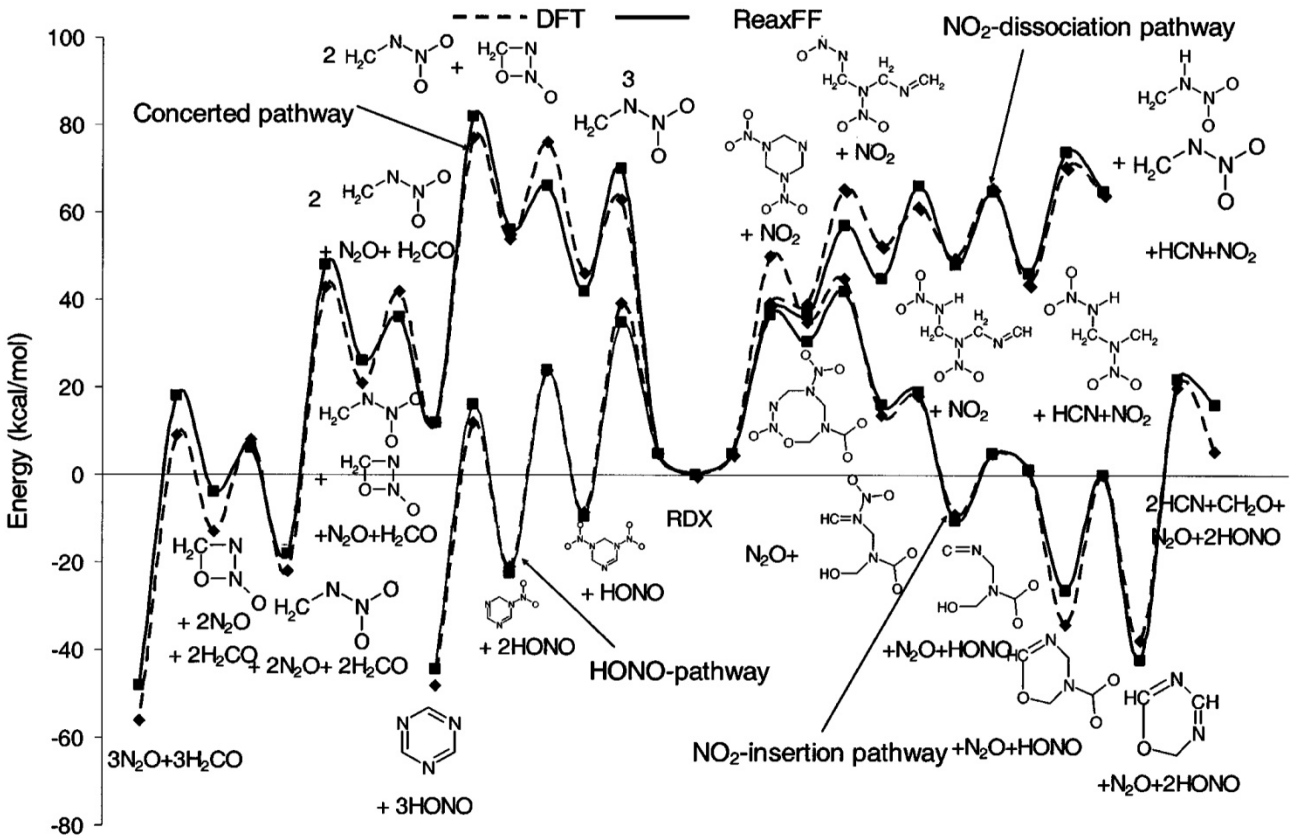
-Parallel ReaxFF: Part of LAMMPS (http://lammps.sandia.gov/)

- Simulation sizes up to a half million atoms on 510 CPU (2 GHz, 8GB per node) (Quenneville, 2006)

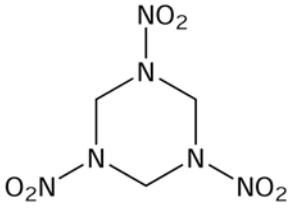
2008: Simulations > 1 million atoms possible with sweetspot of about 5000 atoms per CPU
Additional improvement with new ReaxFF version in LAMMPS expected

ReaxFF/*Ab Initio* Comparison

ReaxFF can decribe a wide variety of chemical reactions.



e.g., unimolecular decomposition of RDX



Strachan, et al, *JCP*, 122, 054502 ('05).

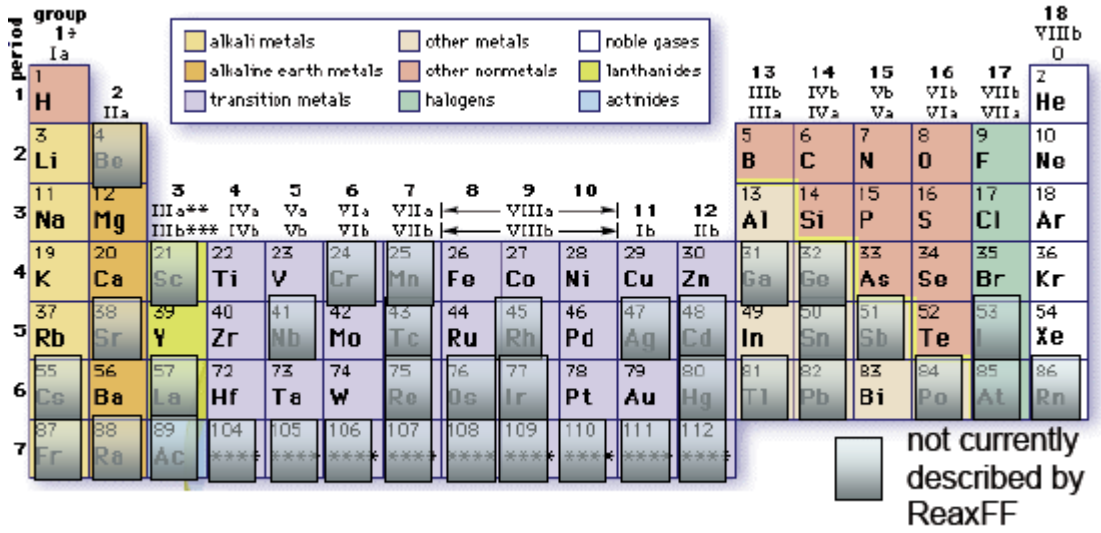
(Original slide from Quenneville presentation)

Part II: ReaxFF as Reactive Force Field

Application Possibilities

http://www.mne.psu.edu/vanduin/distributions.html

For example: proteins, metal systems, fuel cells and combustion



Status 2008 based on description at Interatomic Potentials Workshop 2008

Selection of published ReaxFF parameters and applications (Interatomic Potential Workshop 08, Oxford

- **H/C/O:** - van Duin, Dasgupta, Lorant and Goddard, JPC-A 2001, 105, 9396 (original ReaxFF)
  - Chenoweth, van Duin and Goddard, JPC-A 2008 (combustion)
- **Si/SiO2/SiC** - Buehler, Tang, van Duin and Goddard, PRL 2007, 90, 165502. (crack popagation)
- **High energy** - Nomora, Kalia, Nakano, Vashista, van Duin and Goddard PRL 2007. 99, 148303. (parallel ReaxFF)
- **Al/Al2O3** - Zhang, Cagin, van Duin, Goddard, Qi and Hector, PRB 2004,69,045423
- **Ni/Cu/Co/C** - Su, Nielsen, van Duin and Goddard, PRB 75, 2007
- **Pt/PtH/PtC** (fuel cell anode) - Ludwig, Vlachos, van Duin and Goddard, JPC-B 2006
  - Sanz-Navarro, Astrand, Chen, Ronning, van Duin, Jacob and Goddard, JPC-A 2008
- **Na/Al/Mg/H** - Cheung, Deng, van Duin and Goddard, JPC-A 2005, 109, 851
  - Ojwang, van Santen, Kramer, van Duin and Goddard, JCP 2008.
- **B/N -** Han, Kang, Lee, van Duin and Goddard, JCP 2005, 123,114703
  - Han, Kang, Lee, van Duin and Goddard, JCP 2005, 123,114704
- **Li/LiC** - Han, van Duin and Goddard, JPC-A 2005, 109, 4575
- **Mo/V/Bi/O/C/H** - Goddard et al Topics in Catalysis 2006, 38 (1-3) 93-103.
  - Chenoweth, van Duin, Oxgaard, Cheng and Goddard, accepted in JPC-A.
- **Cu/Zn/O/H** - Raymand, van Duin, Baudin and Hermannsson, Surface Science 2008
  - van Duin et al., in preparation.
- **Y/Zr/Ba/O/H** - van Duin,, Merinov, Jang. and Goddard, W.A. JPC-A 2008. (fuel cell membrane)
  - van Duin, Merinov, Han, Dorso, Goddard, W.A. accepted in JPC-A

Difference reactive/non reactive

Non reactive:

- Can be parameterized to describe structures and energies close to equilibrium
- Expansion with anharmonic terms improves reliability and application range
- Does not dissociate bonds properly
- Often potential is build up as sum of bonded and non bonded interactions with following contributions (bonds+bends+torsions)+(Coulomb+VdW)

Bonded Non bonded

ReaxFF Potential Energy Function

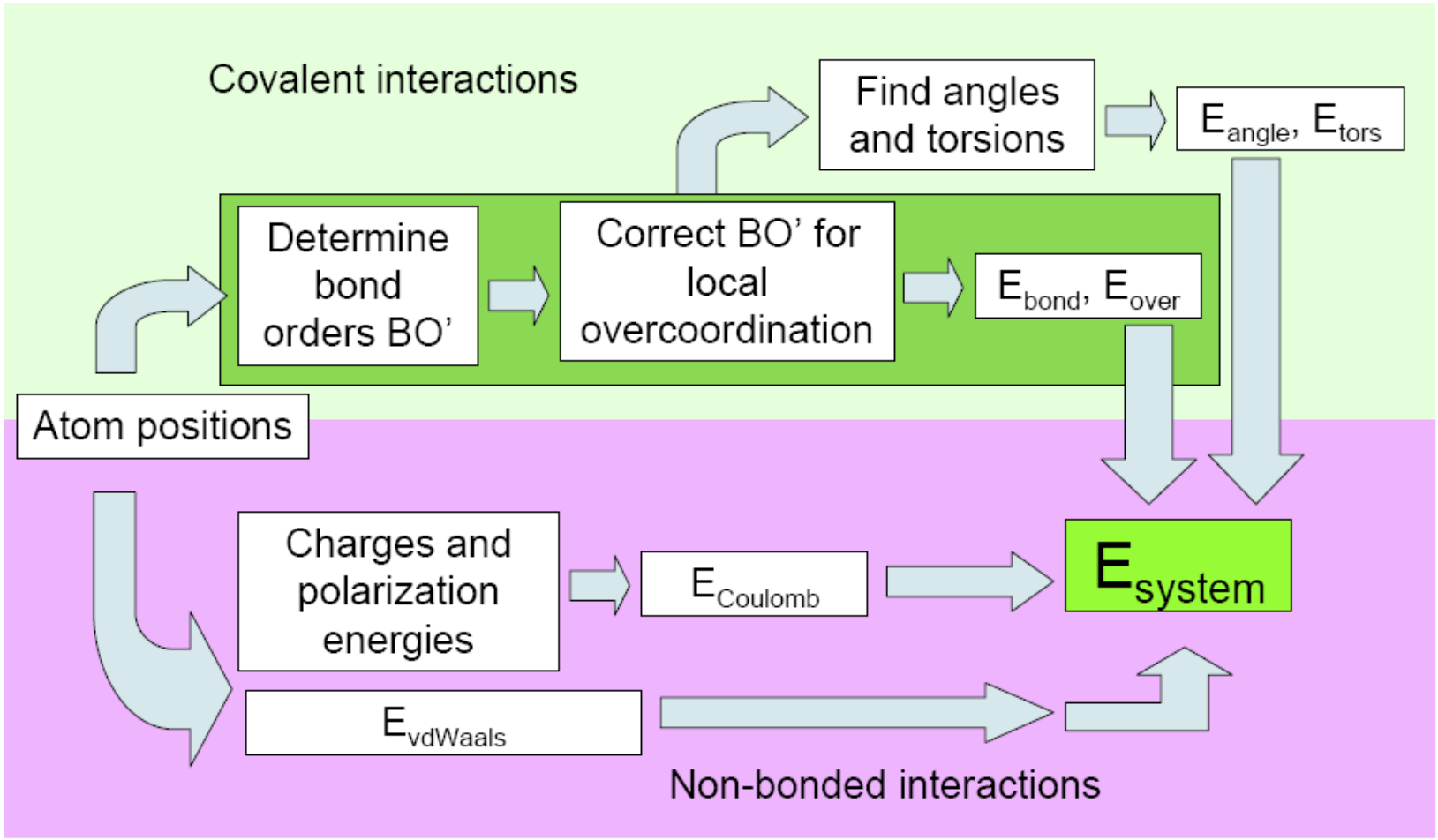
$$E_{system} = E_{bond} + E_{lp} + E_{over} + E_{under} + E_{val} + E_{pen} + E_{coa} + E_{C2} + E_{triple} + E_{tors} + E_{conj} + E_{H\text{-}bond} + E_{vdWaals} + E_{Coulomb}$$

- 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 (H2C=C=CH2)
- E_{coa} : Angle conjugation; stabilizes –NO2 groups
- E_{C2} : C2 correction: destabilizes C=C
- E_{triple} : triple bond related, first mentioned in publications from 2008
- E_{tors} : Torsion energy: bond-order dependent V2-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

ReaxFF general energy terms

- Covalent material: $E_{system} = E_{bond} + E_{over} + E_{val} + E_{tors} + E_{vdWaals} + E_{Coulomb}$
- Metal alloys: $E_{system} = E_{bond} + E_{over} + E_{vdWaals} + E_{Coulomb}$
- Metals: $E_{system} = E_{bond} + E_{over} + E_{vdWaals}$
- Ionic Material: $E_{system} = E_{Coulomb} + E_{vdWaals}$
- Noble Gases: $E_{system} = E_{vdWaals}$

ReaxFF flow diagram



ReaxFF – Key features

- To get a smooth transition from nonbonded to single, double and triple bonded systems ReaxFF employs a bond length/bond order relationship [1,2]. Bond orders are updated every iteration.

- All connectivity-dependent interactions (i.e. valence and torsion angles) are made bond-order dependent, ensuring that their energy contributions disappear upon bond dissociation.

- Nonbonded interactions (van der Waals, Coulomb) are calculated between every atom pair, irrespective of connectivity. Excessive close-range nonbonded interactions are avoided by shielding.

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

1:Tersoff, PRB 1988
2: Brenner, PRB 1990

Bond Order Scheme

Uncorrected bond orders derived from interatomic distances, distinguished between sigma, pi and double pi bonds

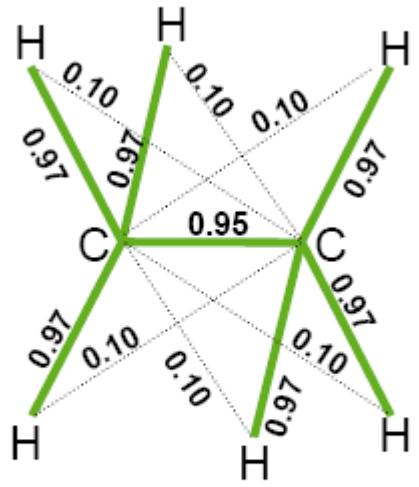
$$BO'_{ij} = BO^{\sigma}_{ij} + BO^{\pi}_{ij} + BO^{\pi\pi}_{ij} = \exp\left[p_{bo1}\cdot\left(\frac{r_{ij}}{r^{\sigma}_{o}}\right)^{p_{bo2}}\right] + \exp\left[p_{bo3}\cdot\left(\frac{r_{ij}}{r^{\pi}_{o}}\right)^{p_{bo4}}\right] + \exp\left[p_{bo5}\cdot\left(\frac{r_{ij}}{r^{\pi\pi}_{o}}\right)^{p_{bo6}}\right]$$

Bond order correction: - in order to avoid over coordination

Mathematical describtion: supplemental information of Chenoweth, K., et al., *The Journal of Physical Chemistry A, 112(5):1040 – 1053*

Bond Order Correction

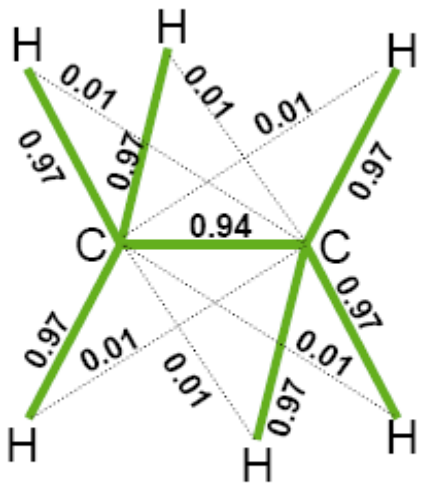
Uncorrected bond orders



$\Sigma BO_C = 4.16$

$\Sigma BO_H = 1.17$

Corrected bond orders

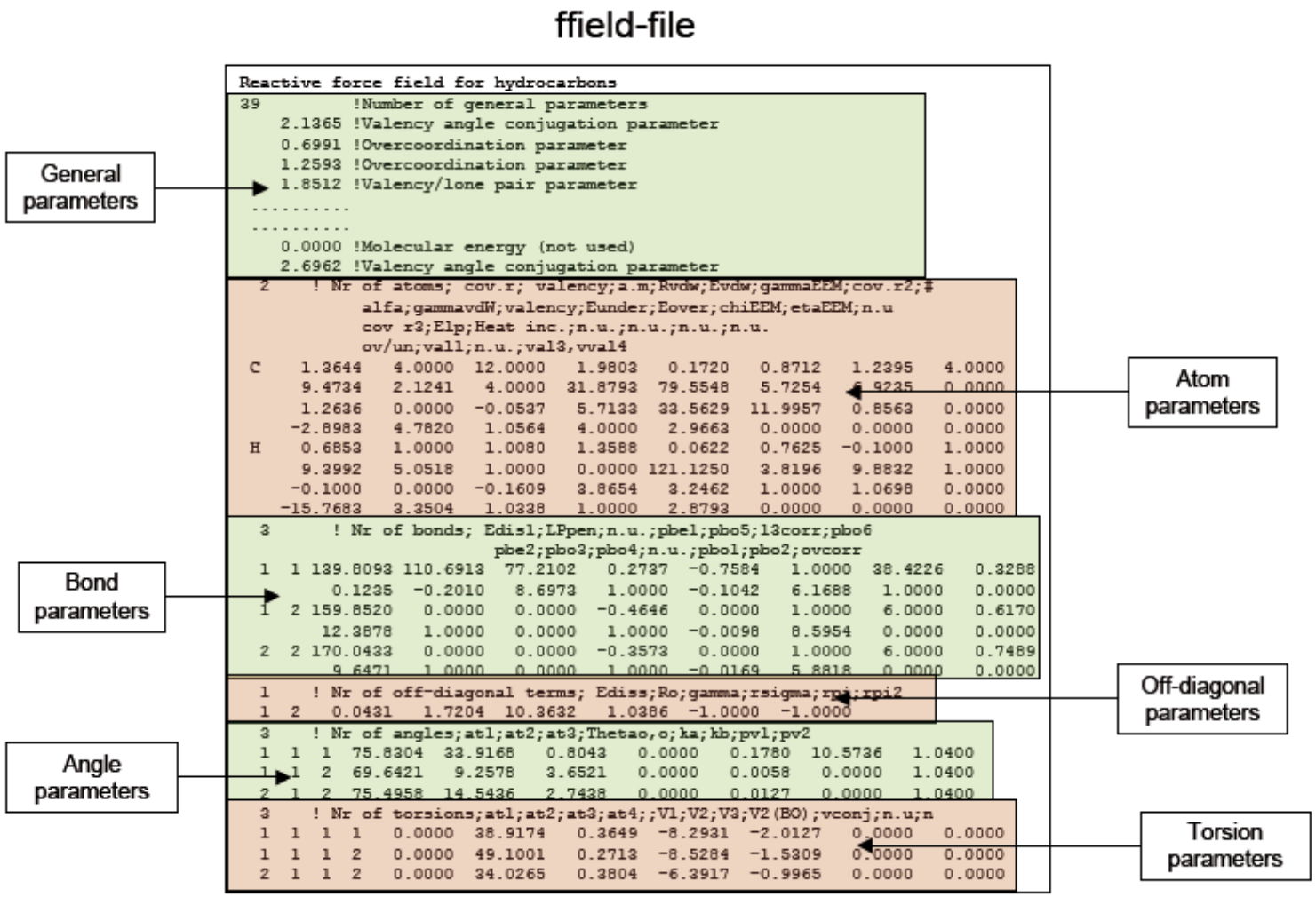


$\Sigma BO_C = 3.88$

$\Sigma BO_H = 0.98$

Idea: remove unrealistic weak bonds, leave strong bonds intact
-> overcoordination disappears

How to create awareness for a new chemical environment



How to create awareness for a new chemical environment

Steps:

1. Atom type description (only for types which have not yet been parameterized)
2. Description of Structures:
   means: declare all possible bond types and related data which can occur during simulation, otherwise the simulation fails
3. Fit the force field sections:
   bond dissociation for wanted types
   introduce the potential for angles
   describe reaction coordinates
4. Optional: include charges for key atoms, vibration frequencies for crystal structures, …

Concept

- build a QM-based database (training set) that described 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
  - Bond dissociation
  - Angle bending
  - Under/overcoordination
  - Key reactions, including transition states
  - Charges
  - Condensed phase data: Equations of state, heats of formation (experiment)

Example 1: Bond dissociation

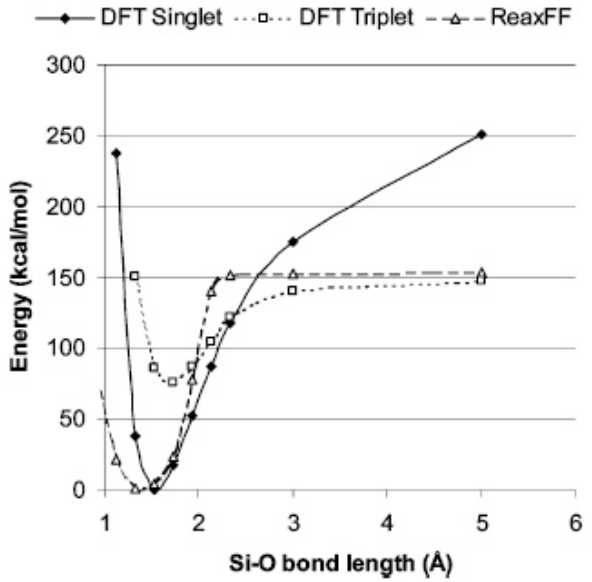


Figure 6. Dissociation of the Si—O double bond in $H_2Si{=}O$.

DFT ReaxFF

Description in trainset.in

- *50.0 + H2SiO opt/1 - H2SiO b1 13/1 -237.90*
- *50.0 + H2SiO opt/1 - H2SiO b1 33/1 -0.01*
- *50.0 + H2SiO opt/1 - H2SiO b1 53/1 -38.10*
- *50.0 + H2SiO opt/1 - H2SiO b1 73/1 -17.90*
- *50.0 + H2SiO opt/1 - H2SiO b1 93/1 -51.90*
- *50.0 + H2SiO opt/1 - H2SiO b2 13/1 -86.90*
- *50.0 + H2SiO opt/1 - H2SiO b2 33/1 -117.50*
- *5.0 + H2SiO opt/1 - H2SiO b4 93/1 -147.20*

(van Duin, A. C. T., et al. 2003, *JPC A, 107:3803 – 3811*
ReaxFFSiO Reactive Force Field for Silicon and Silicon Oxide Systems.)

Interplay with params file: this file defines the section of the force field which should updated using the data provided in trainset.in

Example 2: Valence Angle

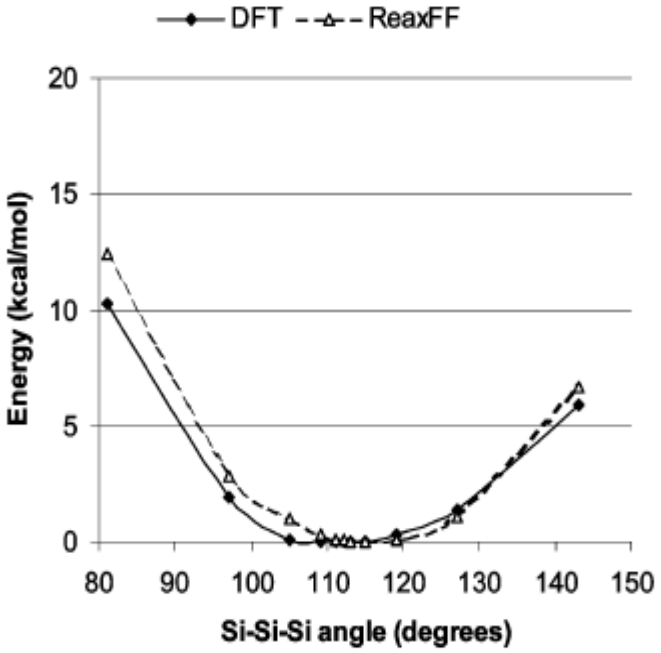


Figure 8. Adiabatic energy of $H_3Si-SiH_2-SiH_3$ as a function of the Si−Si−Si valence angle.

Description in trainset.in

Estimated from figure

```
# Si-Si-Si_angle
0.5    +  a5_7 /1  -  a5_1 /1     -10.40
0.25   +  a5_7 /1  -  a5_2 /1      -3.00
0.25   +  a5_7 /1  -  a5_3 /1      -0.30
0.25   +  a5_7 /1  -  a5_4 /1      -0.40
0.25   +  a5_7 /1  -  a5_5 /1      -0.01
0.25   +  a5_7 /1  -  a5_6 /1      -0.01
0.25   +  a5_7 /1  -  a5_8 /1      -0.20
0.25   +  a5_7 /1  -  a5_9 /1      -0.90
0.25   +  a5_7 /1  -  a5_10/1      -3.90
0.5    +  a5_7 /1  -  a5_11/1      -6.40
```

(van Duin, A. C. T., et al. 2003, *JPC A, 107:3803 – 3811*
ReaxFFSiO Reactive Force Field for Silicon and Silicon Oxide Systems.)

Interplay with params file: this file defines the section of the force field which should updated using the data provided in trainset.in

params

general concept
section element entry in/decrease ratio and finally search domain defined by min and max

Example from CHO force field development:

```
1 4  1  0.2500                                  ! general
…
 2  1  1  0.0050     1.2    1.7                 !C atom parameters
 2  1  4  0.0050     1.6    2.1
...
 3  1  1  1.0000    80.0   250.0                !C-C bond
 3  1  2  1.0000    80.0   250.0
…
  5  1  1  0.2500   5.0000 100.0000             !C-C-C equilibrium angle
  5  1  2  0.2500   5.0000  45.0000
  5  1  3  0.2500   0.1000   7.0000
  5  1  5  0.2500   0.0050   3.0000
  5  1  6  2.5000   0.1000  70.0000
  5  1  7  0.2500   1.0010   3.0000
…
  6  1  1  0.2500    -0.25  2.5                 !C-C-C-C torsion
  6  1  2  5.0000     5.0  80.0
  6  1  3  0.1000    -1.0   1.0
  6  1  4  0.1000     -2.5  -9.0
  6  1  5  0.1000  -3.00    -1.000
```

trainset.in

```
CHARGE
#Iden Weight Atom Lit
chexane 0.1 1 -0.15
ENDCHARGE
HEATFO
#Iden Weight Lit
methane 2.00 -17.80 !Heat of formation
ENDHEATFO
GEOMETRY
#Iden Weight At1 At2 At3 At4 Lit
chexane 0.01 1 2 1.54 !bond
chexane 1.00 1 2 3 111.0 !valence angle
chexane 1.00 1 2 3 4 56.0 !torsion angle
chexane 1.00 0.01 !RMSG
ENDGEOMETRY
CELL PARAMETERS
#Iden Weight Type Lit
chex_cryst 0.01 a 11.20
END CELL PARAMETERS
ENERGY
#Weigh op1 Ide1 n1 op2 Ide2 n2 Lit
#alfa vs. beta vs. gamma cleavage in butylbenzene
1.5 + butbenz/1 - butbenz_a/1 -90.00
ENDENERGY
```

KEYWORDS – I am unaware of the complete set since it has been extended since 2002

Example from user manual dating back to 2002

Training results

- For the presented training set:

		FField value	QM/Lit value	Weight	Error	Total error
methane	Heat of formation:	-17.8000	-17.8000	2.0000	0.0000	0.0000
chexane	Charge atom: 1	-0.1604	-0.1500	0.1000	0.0109	0.0109
Heat of formation:		-29.4900	-29.4900	2.0000	0.0000	0.0109
Bond distance:	1 2	1.5586	1.5400	0.0100	3.4571	3.4679
Bond distance:	1 7	1.1696	1.1000	0.0200	12.1227	15.5906
Bond distance:	1 8	1.1713	1.1000	0.0200	12.7203	28.3109
Valence angle:	1 2 3	110.8117	111.0000	1.0000	0.0354	28.3463
Valence angle:	7 1 8	104.3207	107.0000	1.0000	7.1788	35.5251
chex_cryst	a:	11.8448	11.2000	0.4000	2.5987	38.1238
Energy +butbenz/ 1 -butbenz_a/ 1		-96.6941	-90.0000	1.5000	19.9158	58.0396
Energy +butbenz/ 1 -butbenz_b/ 1		-63.4751	-71.0000	1.5000	25.1663	83.2060
Energy +butbenz/ 1 -butbenz_c/ 1		-77.1805	-78.0000	1.5000	0.2985	83.5045

$$Error^{ReaxFF}=\{[v^{ReaxFF}-v^{QC/Lit}]/weight\}^2$$

Simulations and output of Standalone ReaxFF

(Lammps is limited to its own output files)

- General output files:

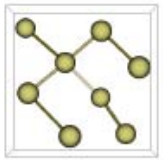
- Connection table (fort.7, fort.8)
- Trajectory (xmolout)
- Molecular composition (molfra.out)
- run.log (generated by exe-script)
- output geometry in .bgf (fort.90, $DESCRP.bgf), .geo (fort.98, $DESCRP.geo), MOPAC (output.MOP) and .pdb (output.pdb) formats

Examples from NASA Ames workshop 2006

- Si particle oxidation
- Si-unit cell minimization
- Creation of a 216-atom supercell
- Creation of a Si216-cluster
- Si216-equilibration at T=500K
- MD-anneal simulation of Si216-cluster
- Addition of O2: equilibration at T=1000K
- NVE-simulation of Si216-particle oxidation
- Si-surface impact on SiO2/Si
- Force field development

The following slides are taken from the original presentation,

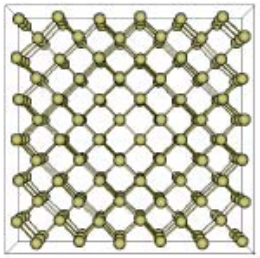
Si-particle oxidation



8-atom Si(alfa) unit cell
(Si_unit_minim)

Minimization + supercell construction

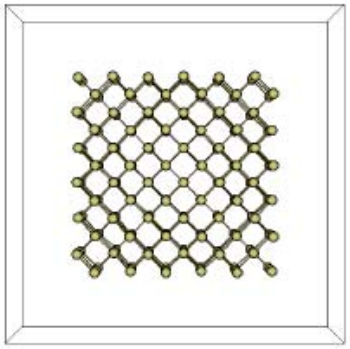
t_{cpu}<<1 sec.



216-atom Si(alfa) super cell
(Si_supercell_minim)

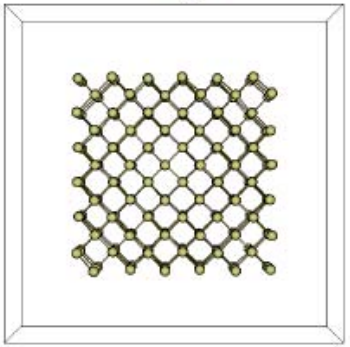
Minimization + cell boundary extension

t_{cpu}<1 sec.



Si_{216}-cluster
(Si216_cluster_minim)

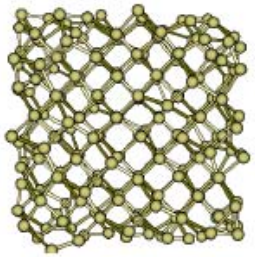
Minimization



MD-NVT 500K
(Si216_cluster_MD_500K)

Equilibrate system at T=500K

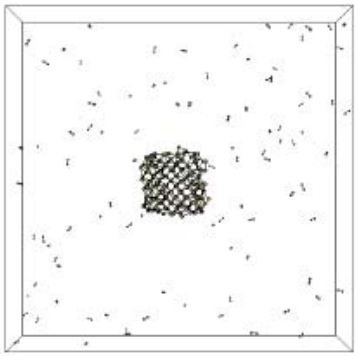
t_{cpu}=506 sec.
5000 iterations



Anneal cluster
(Si216_cluster_1750K_anneal)

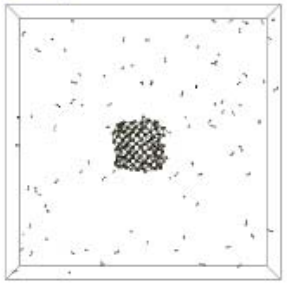
Heat up and cool down to generate stable cluster

t_{cpu}=19758 sec.
100,000 iterations



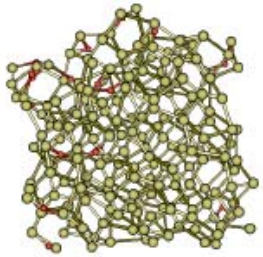
Add O_2-gas; MD-NVT 1000K
(Si216_annealed_O2_1000K)

t_{cpu}=500 sec.
3000 iterations



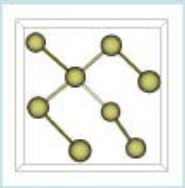
Switch on Si-O bond; NVE-simulation
(Si216_annealed_O2_NVE)

250,000 iterations



Oxidized Si-particle

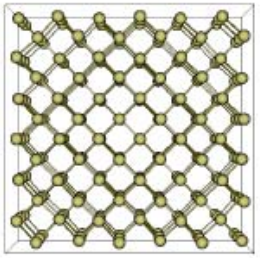
Si(alfa) unit cell minimization



8-atom Si(alfa) unit cell
(Si_unit_minim)

Minimization + supercell construction

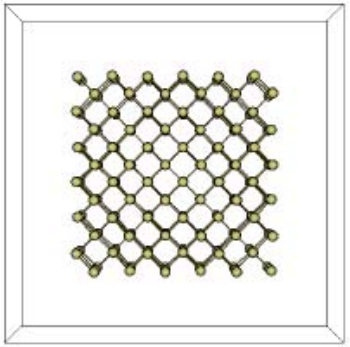
t_{cpu}<<1 sec.



216-atom Si(alfa) super cell
(Si_supercell_minim)

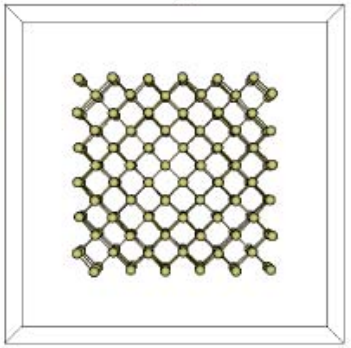
Minimization + cell boundary extension

t_{cpu}<1 sec.



Si_{216}-cluster
(Si216_cluster_minim)

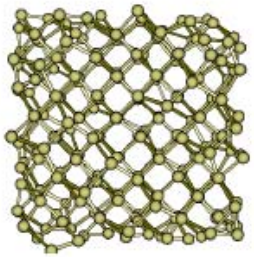
Minimization



MD-NVT 500K
(Si216_cluster_MD_500K)

Equilibrate system at T=500K

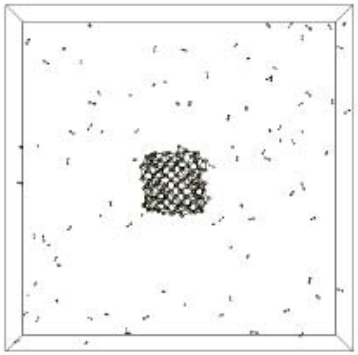
t_{cpu}=506 sec.
5000 iterations



Anneal cluster
(Si216_cluster_1750K_anneal)

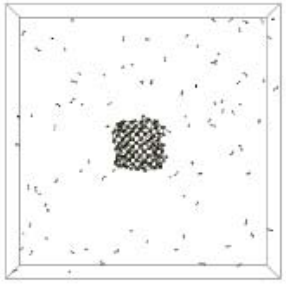
Heat up and cool down to generate stable cluster

t_{cpu}=19758 sec.
100,000 iterations



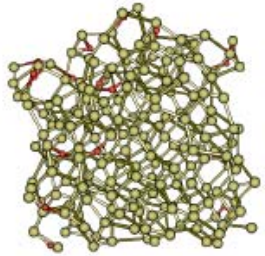
Add O_2-gas; MD-NVT 1000K
(Si216_annealed_O2_1000K)

t_{cpu}=500 sec.
3000 iterations



Switch on Si-O bond; NVE-simulation
(Si216_annealed_O2_NVE)

250,000 iterations



Oxidized Si-particle

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
```

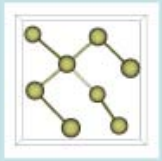
geo

```
# General parameters
    2 iexx      Nr. of unit cells in x-direction to fort.85
    2 iexy      Nr. of unit cells in y-direction to fort.85
    2 iexz      Nr. of unit cells in z-direction to fort.85
    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
    1 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

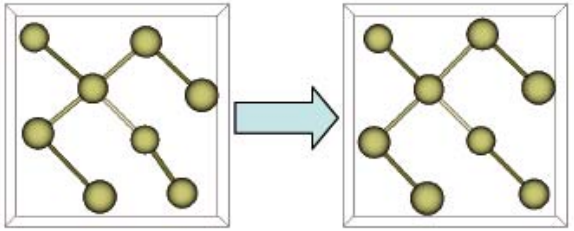
- Other input files : exe, ffield (standard)



Minimization + supercell construction

8-atom Si(alfa) unit cell t_{cpu}<<1 sec.
(Si_unit_minim)

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

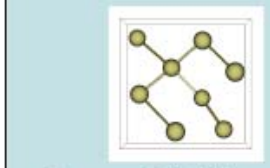
```
F a_Si_opt
  16.1116   16.1116   16.1116
  90.0000   90.0000   90.0000
   1 Si   0.201308156929372E+01 0.469899935734249E+01 0.469807931385440E+01
   2 Si   0.335759198919583E+01 0.335587406316292E+01 0.670911888011277E+00
   3 Si   0.470033249708392E+01 0.469958237639442E+01 0.201445663138070E+01
   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 0.114130587516990
```

fort.85

Extended unit cell (xyz-format)

Other output files:

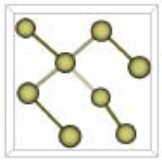
- fort.7, fort.8: connection table
- fort.58: partial energies
- fort.73: final partial energies
- fort.90: final geometry (.bgf)
- xmolout: .xyz coordinates
- molfra.out : system composition
- summary.txt: summary simulation



Minimization + supercell construction

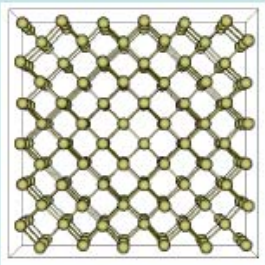
8-atom Si(alfa) unit cell t_{cpu}<<1 sec.
(Si_unit_minim)

216-atom super cell minimization



8-atom Si(alfa) unit cell t_{cpu}<<1 sec.
(Si_unit_minim)

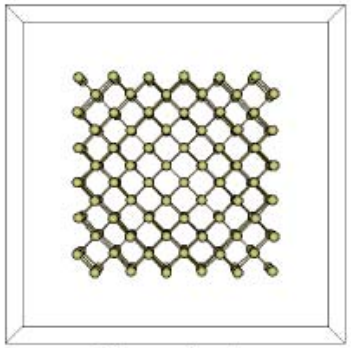
Minimization + supercell construction



216-atom Si(alfa) super cell
(Si_supercell_minim)

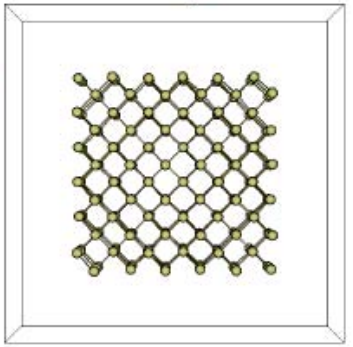
Minimization + cell boundary extension

t_{cpu}<1 sec.



Si_{216}-cluster
(Si216_cluster_minim)

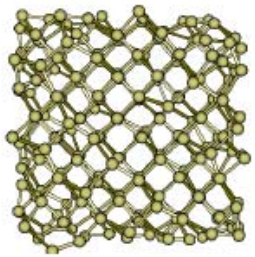
Minimization



MD-NVT 500K
(Si216_cluster_MD_500K)

Equilibrate system at T=500K

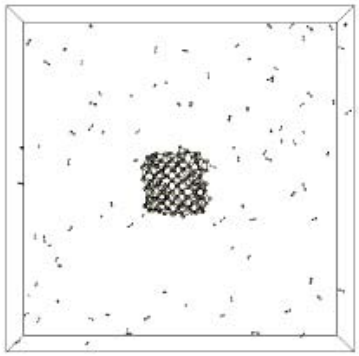
t_{cpu}=506 sec.
5000 iterations



Anneal cluster
(Si216_cluster_1750K_anneal)

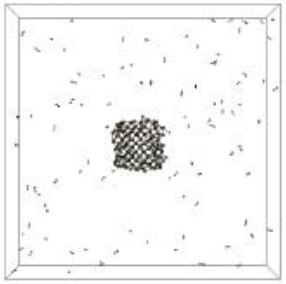
Heat up and cool down to generate stable cluster

t_{cpu}=19758 sec.
100,000 iterations



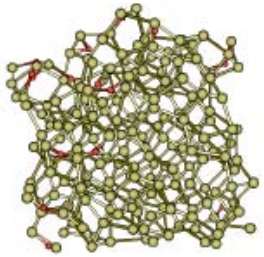
Add O_2-gas; MD-NVT 1000K
(Si216_annealed_O2_1000K)

t_{cpu}=500 sec.
3000 iterations



Switch on Si-O bond; NVE-simulation
(Si216_annealed_O2_NVE)

250,000 iterations



Oxidized Si-particle

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
```

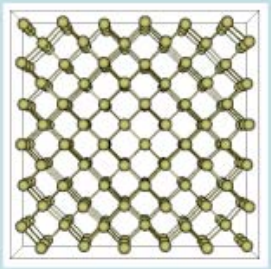
geo (fort.85)

```
# 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)



Minimization + cell boundary extension

t_{cpu}<1 sec.

216-atom Si(alfa) super cell
(Si_supercell_minim)

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

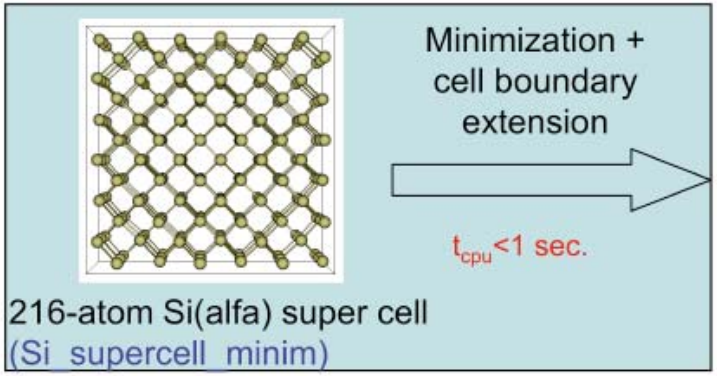
```
XTLGRF 200
DESCRP a_Si_opt
RUTYPE NORMAL RUN
CRYSTX   16.11160  16.11160  16.11160  90.00000  90.00000  90.00000
FORMAT ATOM  (a6,1x,i5,1x,a5,1x,a3,1x,a1,1x,a5,3f10.5,1x,a5,i3,i2,1x,f8.5)
HETATM    1 Si             2.01390  4.69950  4.69915  Si  0 0  0.00000
HETATM    2 Si             3.35655  3.35653  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

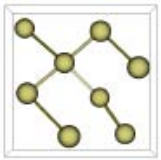
Biograf output-file

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



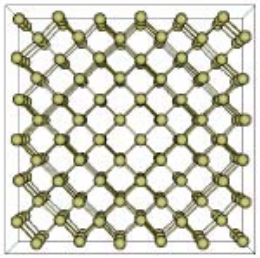
Si_{216}-cluster minimization



8-atom Si(alfa) unit cell
(Si_unit_minim)

Minimization + supercell construction

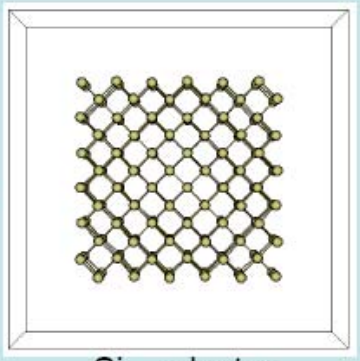
t_{cpu}<<1 sec.



216-atom Si(alfa) super cell
(Si_supercell_minim)

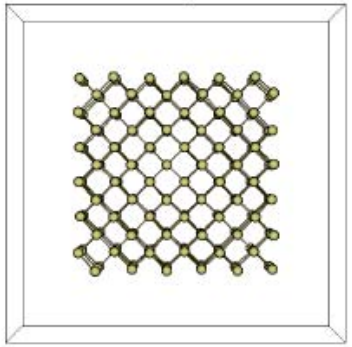
Minimization + cell boundary extension

t_{cpu}<1 sec.



Si_{216}-cluster
(Si216_cluster_minim)

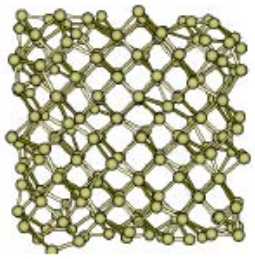
Minimization



MD-NVT 500K
(Si216_cluster_MD_500K)

Equilibrate system at T=500K

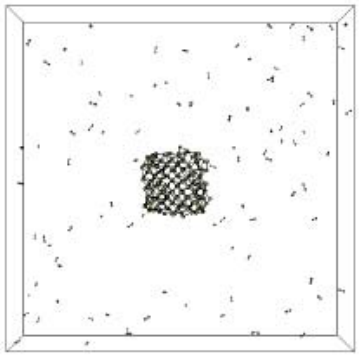
t_{cpu}=506 sec.
5000 iterations



Anneal cluster
(Si216_cluster_1750K_anneal)

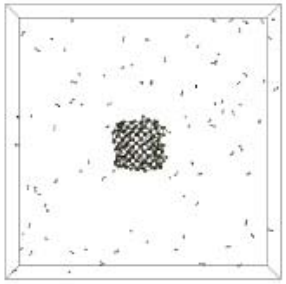
Heat up and cool down to generate stable cluster

t_{cpu}=19758 sec.
100,000 iterations



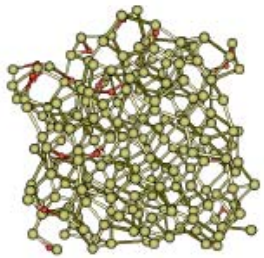
Add O_2-gas; MD-NVT 1000K
(Si216_annealed_O2_1000K)

t_{cpu}=500 sec.
3000 iterations



Switch on Si-O bond; NVE-simulation
(Si216_annealed_O2_NVE)

250,000 iterations



Oxidized Si-particle

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

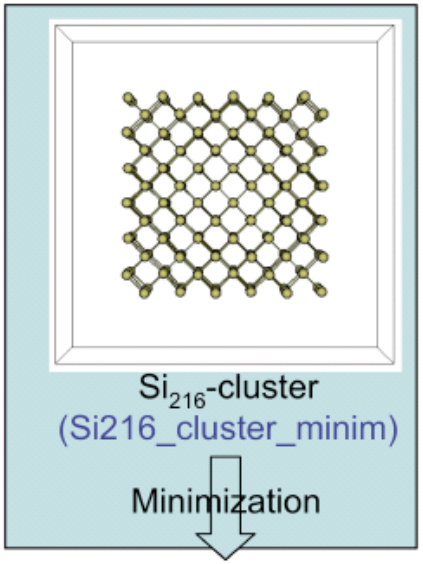
```
# General parameters
    1 icentr    0: use user definitions  1: place system in centre periodic box  2: place...
    1 itrans    0: do not back-translate atoms   1: Translate atoms after crossing....
 02.50 range     Range for back-translation of atoms
    1 imetho    0: Normal MD-run 1: Energy minimisation
    0 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

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

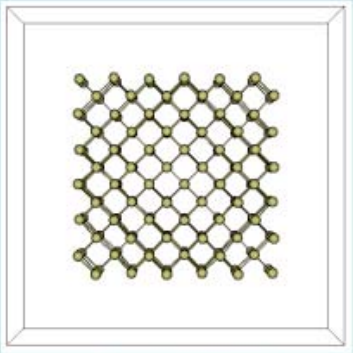
Other output files:
- fort.58: partial energies
- fort.73: final partial energies
- xmolout: .xyz coordinates
- molfra.out : system composition
- summary.txt: summary simulation

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

fort.7

Atom type | Mol# | Sum BO's | Charge

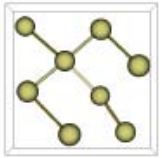


Si_{216}-cluster
(Si216_cluster_minim)

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

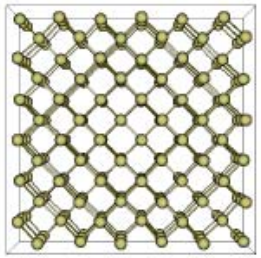
MD-NVT at T=500K on Si_{216}-cluster



8-atom Si(alfa) unit cell
(Si_unit_minim)

Minimization + supercell construction

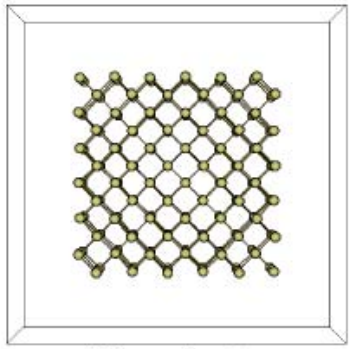
t_{cpu}<<1 sec.



216-atom Si(alfa) super cell
(Si_supercell_minim)

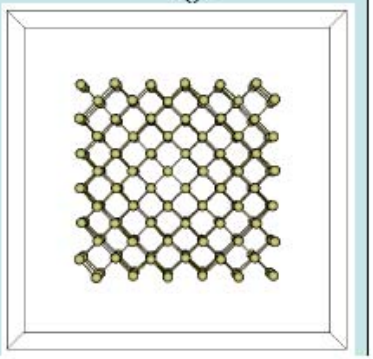
Minimization + cell boundary extension

t_{cpu}<1 sec.



Si_{216}-cluster
(Si216_cluster_minim)

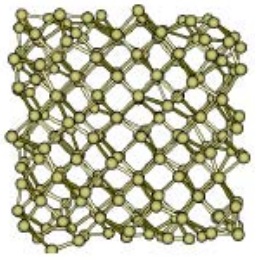
Minimization



MD-NVT 500K
(Si216_cluster_MD_500K)

Equilibrate system at T=500K

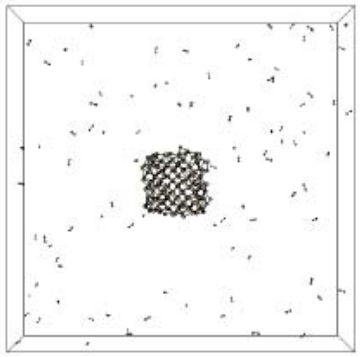
t_{cpu}=506 sec.
5000 iterations



Anneal cluster
(Si216_cluster_1750K_anneal)

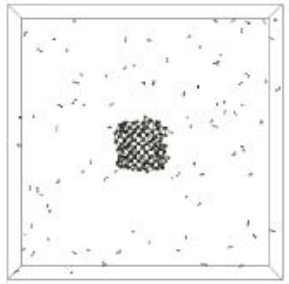
Heat up and cool down to generate stable cluster

t_{cpu}=19758 sec.
100,000 iterations



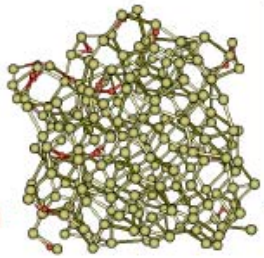
Add O_2-gas; MD-NVT 1000K
(Si216_annealed_O2_1000K)

t_{cpu}=500 sec.
3000 iterations



Switch on Si-O bond; NVE-simulation
(Si216_annealed_O2_NVE)

250,000 iterations



Oxidized Si-particle

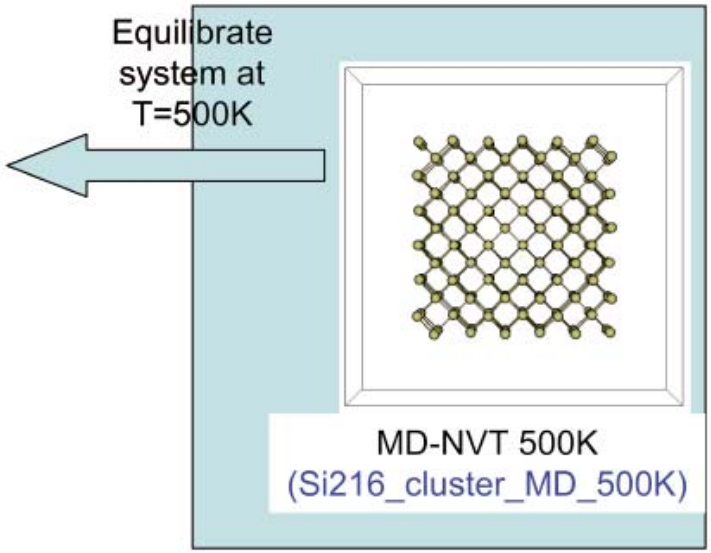
Input files

```
...
     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 cutof2     BO-cutoff for valency angles and torsion angles (do not change)
  0.300 cutof3     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
     1 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:
0005000 nmdit      Number of MD-iterations
  00001 ichupd     Charge update frequency
    005 iout1      Output to unit 71 and unit 73
   0050 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
 001000 iout6      Save velocity file
 000025 irten      Frequency of removal of rotational and translational energy
     0 npreit     Nr. of iterations in previous runs
# MM-parameters
```

Relevant keyword
Default keyword

control

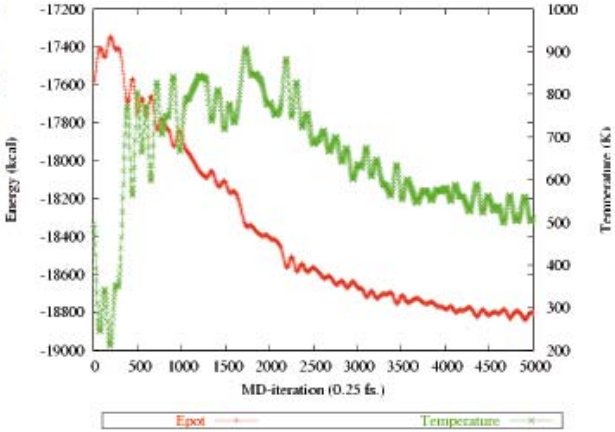
- Other input files : geo,exe, ffield (standard)

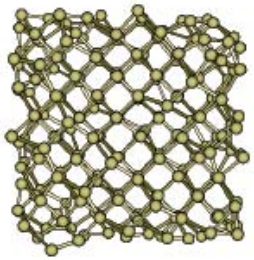


Output files

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

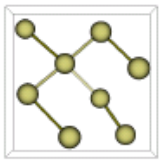




- Potential energy drops as undercoordinated atoms pair up
- Temperature increases due to energy release; thermostat drives temperature back to 500K after locally stable structure is found
- Need to melt the surface to find a more stable structure

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

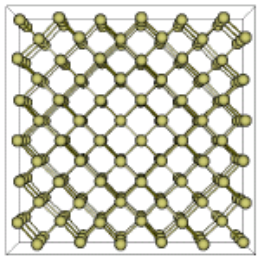
MD-anneal simulation on Si_{216}-cluster



8-atom Si(alfa) unit cell
(Si_unit_minim)

Minimization + supercell construction

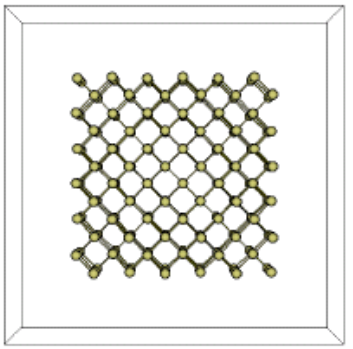
t_{cpu}<<1 sec.



216-atom Si(alfa) super cell
(Si_supercell_minim)

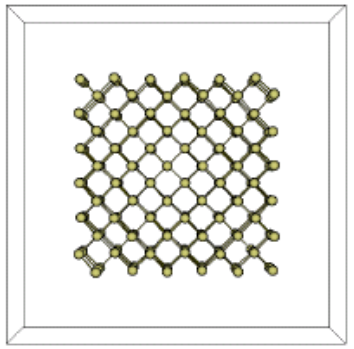
Minimization + cell boundary extension

t_{cpu}<1 sec.



Si_{216}-cluster
(Si216_cluster_minim)

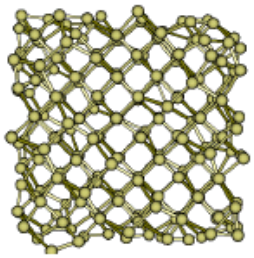
Minimization



MD-NVT 500K
(Si216_cluster_MD_500K)

Equilibrate system at T=500K

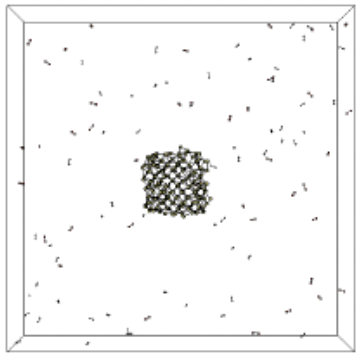
t_{cpu}=506 sec.
5000 iterations



Anneal cluster
(Si216_cluster_1750K_anneal)

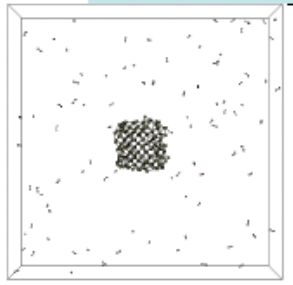
Heat up and cool down to generate stable cluster

t_{cpu}=19758 sec.
100,000 iterations



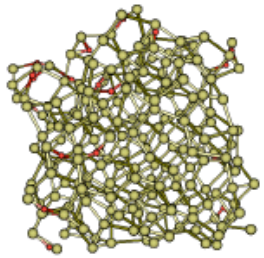
Add O_2-gas; MD-NVT 1000K
(Si216_annealed_O2_1000K)

t_{cpu}=500 sec.
3000 iterations



Switch on Si-O bond; NVE-simulation
(Si216_annealed_O2_NVE)

250,000 iterations



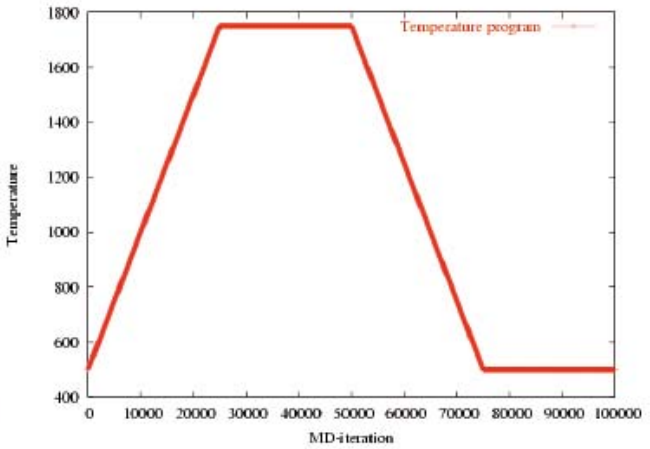
Oxidized Si-particle

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  1 216  500.0   100.0   0.05
25000   1  1 216 1750.0   100.0   0.00
50000   1  1 216 1750.0   100.0  -0.05
75000   1  1 216  500.0   100.0   0.00
```

tregime.in



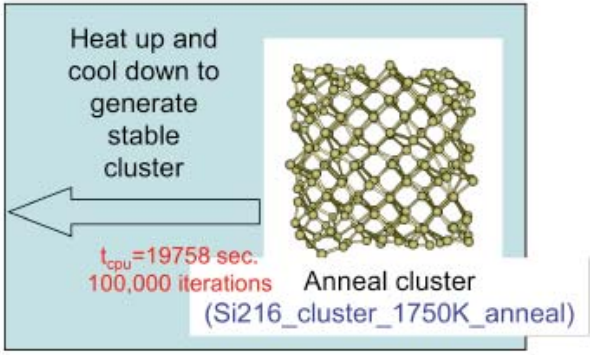
- Temperature program
- Can also define multiple temperature zones (see manual)

```
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
...
...
...
```

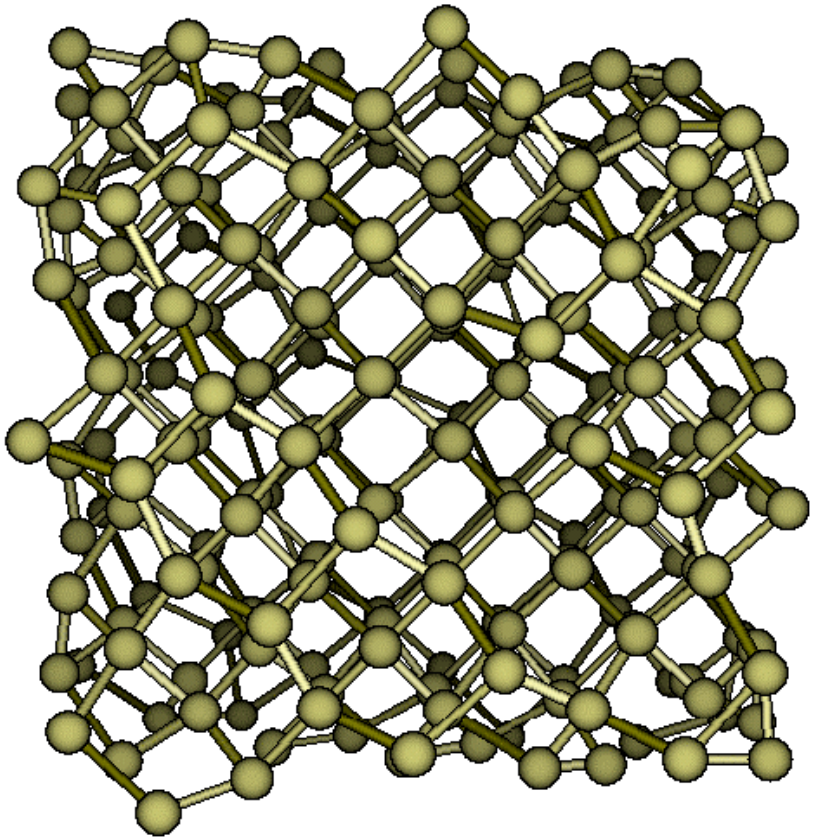
vels (moldyn.vel from 500K-equilibration)

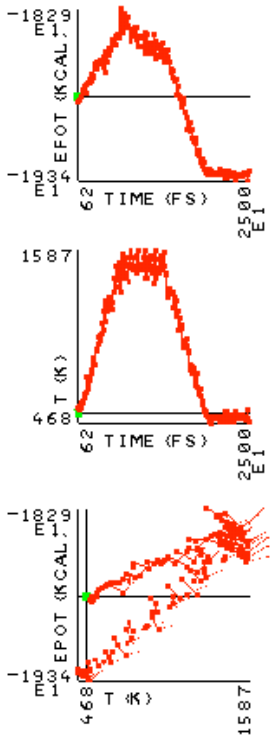
- Other input files : geo,exe, ffield, control (standard)

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



Output files



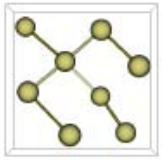


SI 216 MD ANNEAL

Relevant output files :
- fort.75 (expanded temperature information)
- summary.txt
- xmolout
- fort.71
- fort.73
- fort.7

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

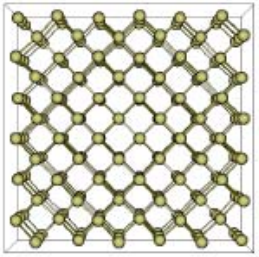
Add 100 O_2-molecules; equilibrate at T=1000K; switch off Si-O bonds



8-atom Si(alfa) unit cell
(Si_unit_minim)

Minimization + supercell construction

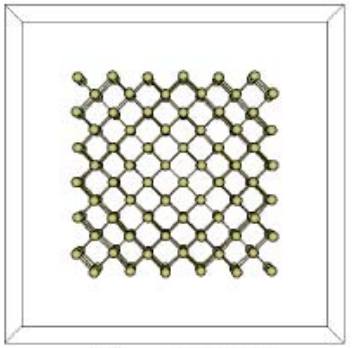
t_{cpu}<<1 sec.



216-atom Si(alfa) super cell
(Si_supercell_minim)

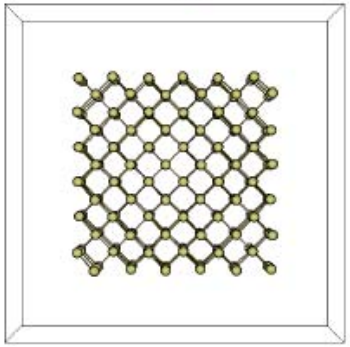
Minimization + cell boundary extension

t_{cpu}<1 sec.



Si_{216}-cluster
(Si216_cluster_minim)

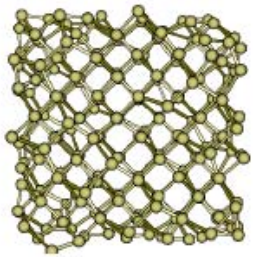
Minimization



MD-NVT 500K
(Si216_cluster_MD_500K)

Equilibrate system at T=500K

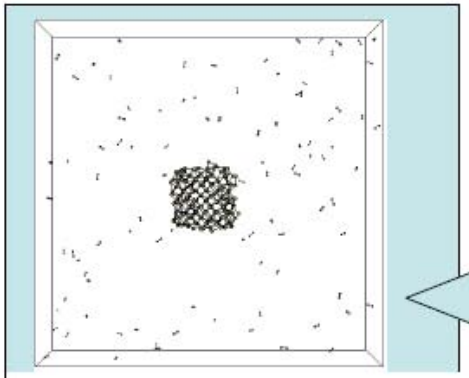
t_{cpu}=506 sec.
5000 iterations



Anneal cluster
(Si216_cluster_1750K_anneal)

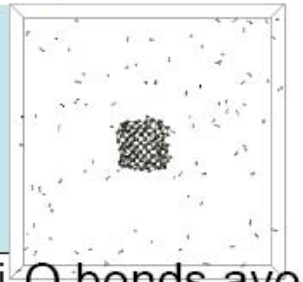
Heat up and cool down to generate stable cluster

t_{cpu}=19758 sec.
100,000 iterations



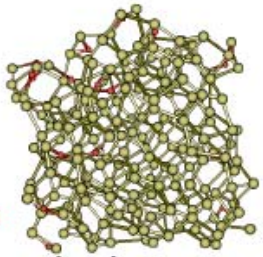
Add O_2-gas; MD-NVT 1000K
(Si216_annealed_O2_1000K)

t_{cpu}=500 sec.
3000 iterations



Switch on Si-O bond; NVE-simulation
(Si216_annealed_O2_NVE)

250,000 iterations



Oxidized Si-particle

- Switching off Si-O bonds avoids reactions during equilibration

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
```

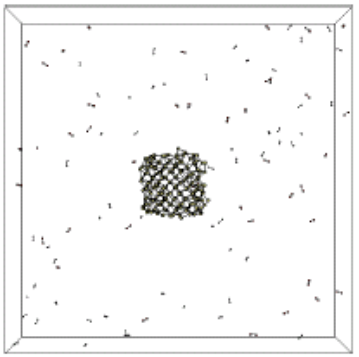
geo

- 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
```

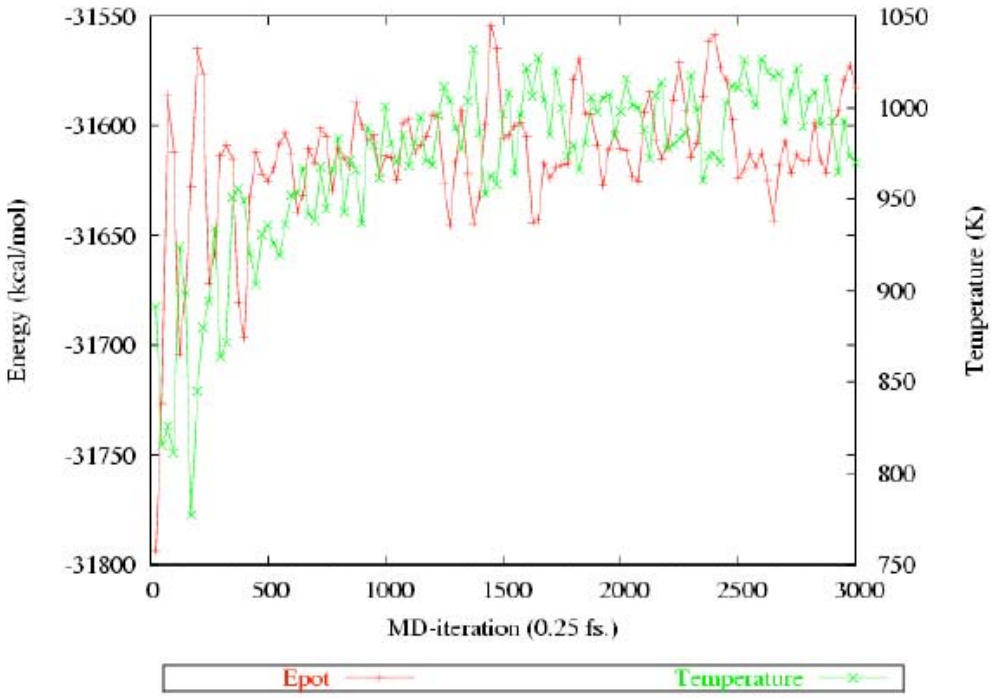
ffield

Modified force field parameter
Default parameter



- Switching off Si-O bonds avoids reactions during equilibration

Output files



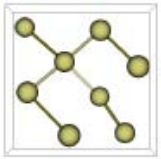
Relevant output files :
- fort.71
- summary.txt
- xmolout
- fort.71
- fort.73
- fort.7
- moldyn.vel

```
Bond order cutoff:0.3000
Iteration Freq. Molecular formula     Molecular mass
    0    100 x  O2                     31.9980
    0      1 x  Si216                  6060.9600
...
...
Iteration Freq. Molecular formula     Molecular mass
 3000 100 x  O2                       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

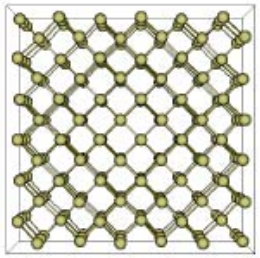
NVE-simulation on Si_{216}-particle/O_2 starting at T=1000K



8-atom Si(alfa) unit cell
(Si_unit_minim)

Minimization + supercell construction

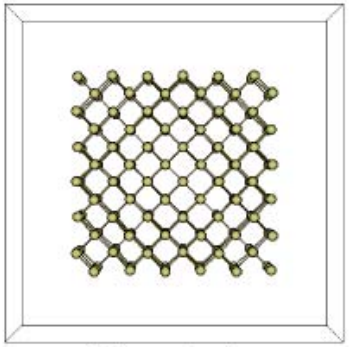
t_{cpu}<<1 sec.



216-atom Si(alfa) super cell
(Si_supercell_minim)

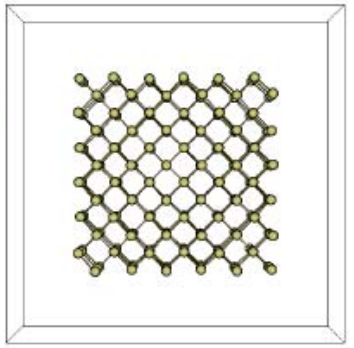
Minimization + cell boundary extension

t_{cpu}<1 sec.



Si_{216}-cluster
(Si216_cluster_minim)

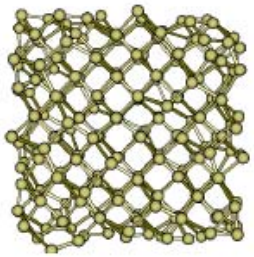
Minimization



MD-NVT 500K
(Si216_cluster_MD_500K)

Equilibrate system at T=500K

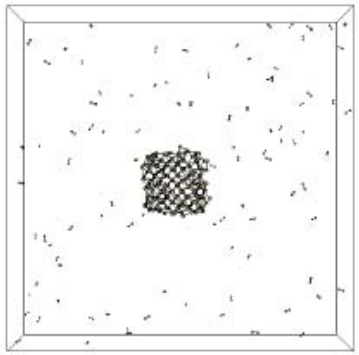
t_{cpu}=506 sec.
5000 iterations



Anneal cluster
(Si216_cluster_1750K_anneal)

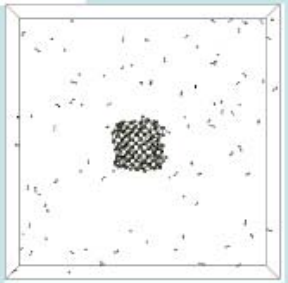
Heat up and cool down to generate stable cluster

t_{cpu}=19758 sec.
100,000 iterations



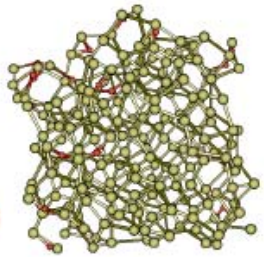
Add O_2-gas; MD-NVT 1000K
(Si216_annealed_O2_1000K)

t_{cpu}=500 sec.
3000 iterations



Switch on Si-O bond; NVE-simulation
(Si216_annealed_O2_NVE)

250,000 iterations



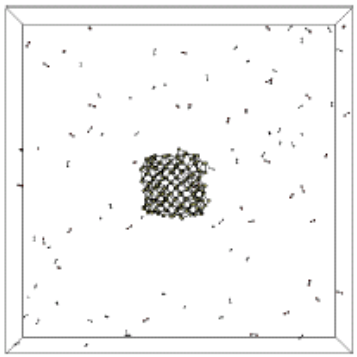
Oxidized Si-particle

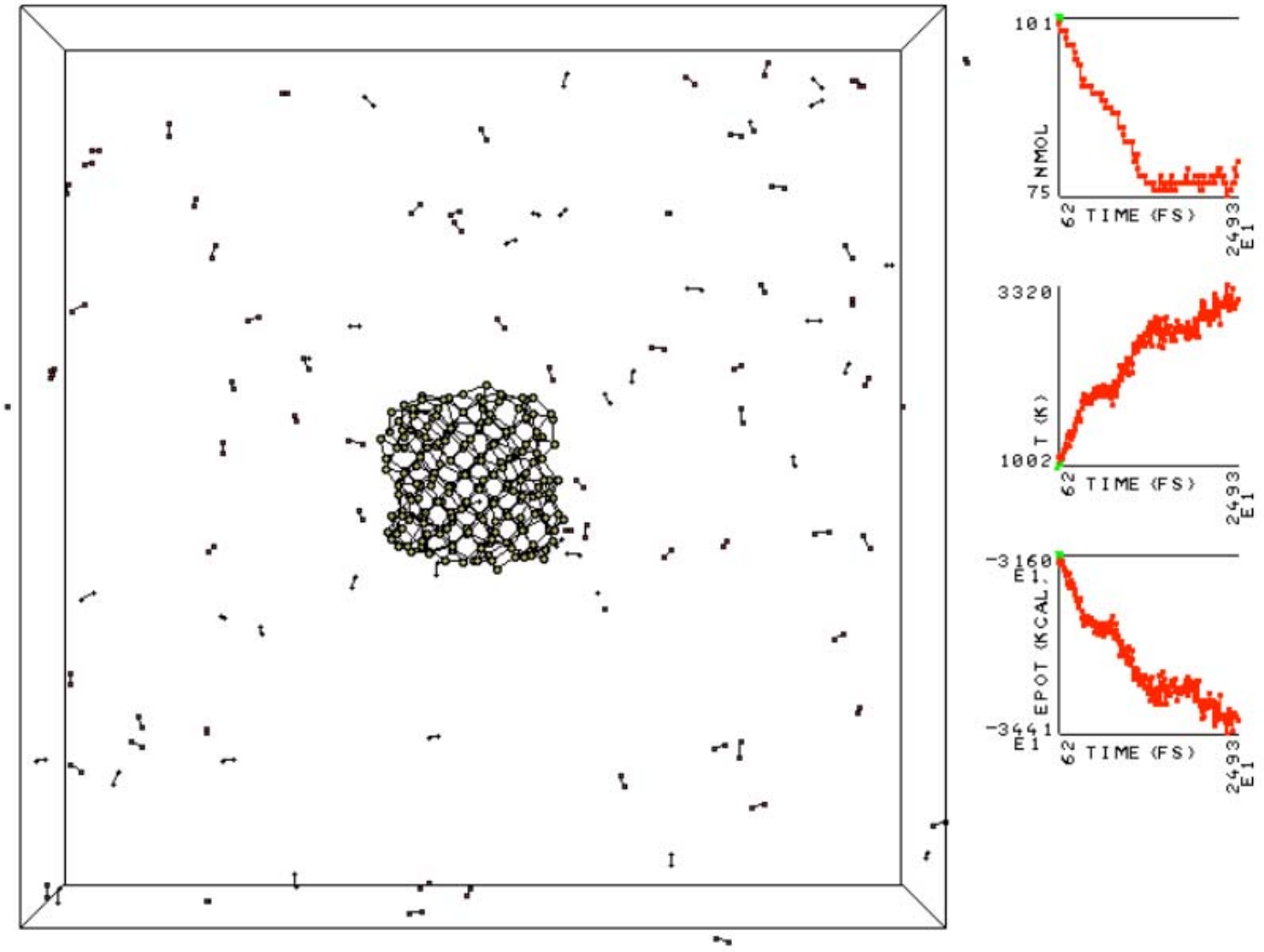
Input files

```
...
     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 cutof2     BO-cutoff for valency angles and torsion angles (do not change)
  0.300 cutof3     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

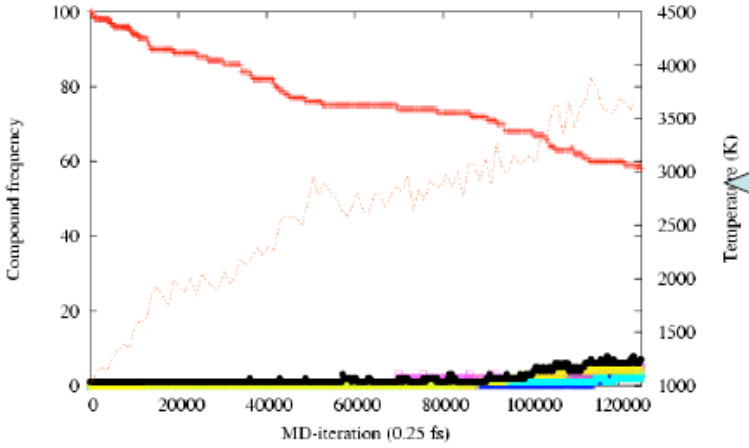
- Copied moldyn.vel from 1000K-equilibration to vels
- Other input files : exe, geo, ffield (standard)

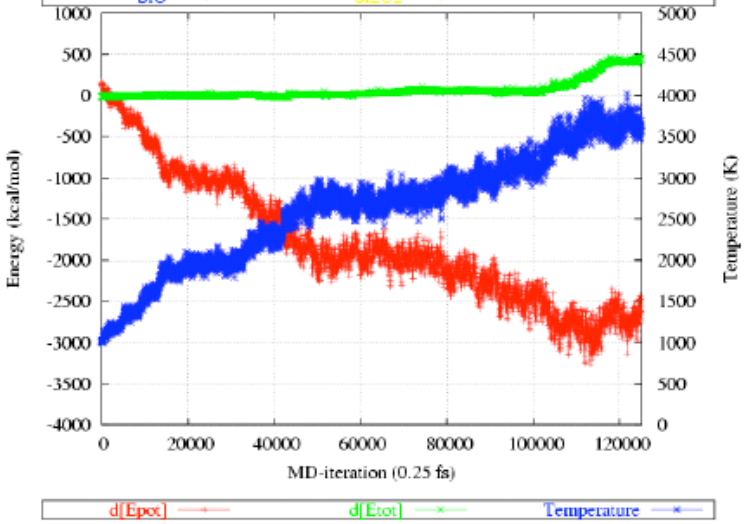




- Highly exothermic reaction
- Temperature rises to >3000K; particle becomes unstable

Output files






```
Bond order cutoff:0.3000
Iteration Freq. Molecular formula      Molecular mass
    0    100 x  O2                     31.9980
    0      1 x  Si216                  6060.9600
...
...
Iteration Freq. Molecular formula      Molecular mass
  125000   1 x  O52Si181                5910.8080
  125000   1 x  O3Si3                   132.1770
  125000  58 x  O2                     31.9980
  125000   3 x  O2Si3                  116.1780
  125000   3 x  OSi                    44.0590
  125000   4 x  O2Si2                  88.1180
  125000   1 x  O2Si                   60.0580
  125000   2 x  OSi2                   72.1190
  125000   2 x  O                      15.9990
  125000   1 x  O3Si2                  104.1170
  125000   1 x  O3                     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

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

Other relevant output files :
- fort.71
- summary.txt
- xmolout
- fort.71
- fort.73
- fort.7
- moldyn.vel