Reactive force fields: concepts of ReaxFF

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Aim: simulation of the dynamics of large, complicated reactive systems

Simulation of the decomposition of a archaeol lipid biomarker by exposure to high-velocity (30eV) N-radicals
Outline

- Energy minimization and molecular dynamics methods
- Simulations on the dynamics of chemical reactions
- How to make a force field reactive: building the ReaxFF reactive force field
  - Concepts of covalent non-reactive force fields
  - Introduction of bond orders
  - Non-bonded interactions in a reactive force field
  - Charge polarization
  - Current status of the ReaxFF method
  - ReaxFF program, in- and output files
- Force field development for Si/SiO systems
- Applications of the Si/SiO reactive force field
  - Hydrogen diffusion in Si/SiO$_2$ interfaces
  - Thermal decomposition of PDMS polymers
Energy minimization (EM) and molecular dynamics (MD) methods

**EM**
- Temperature (=velocity) is zero
- Only sample 1 system configuration

**MD**
- Non-zero temperature
- Sample configurational space; the higher the temperature the more configurations become available
- Energy conservation: $E_{\text{kin}} + E_{\text{pot}} = \text{constant}$
Energy minimization methods: structure

Input structure → Force calculation (QM, FF) → Energy minimizer (Steepest descent, conjugate gradient, Newton-Raphson) → Iterative cycle → Output structure

Have I reached convergence?

Yes → Updated geometry

No → Iterative cycle
MD-methods: structure

Input structure

Update velocities from forces

Force calculation (QM, FF)

Update positions from velocities

Iterative cycle

NVE: do nothing
NVT: rescale velocities to control temperature
NPT: rescale system volume to control pressure
FF energy minimization of a methylphenanthrene radical using a steepest descent method

FF NVE molecular dynamics of a methylphenanthrene radical at T=700K
Applications of EM and MD

EM
- Determine static (0 Kelvin) properties of a single system configuration.
- Can be used to calculate IR, NMR-spectra, geometry information, relative energies.
- Usually employed on a single molecule; not relevant for multi-molecular systems.

MD
- Used to sample the configurational space; average over multiple system configurations.
- Can be used to model temperature and pressure effects
- Can be used to calculate diffusion constants, reaction rates.
- Can be employed on multi-component systems.
- Almost always FF; QM/MD is very expensive
Simulations on the dynamics of chemical reactions

QM methods:
- Fundamental
- Expensive, only small systems

FF methods
- Empirical; need to be trained
- Much cheaper than QM, can be applied to much larger systems
QM-methods

\[ H \Psi = E \Psi \]

\[
H = - \sum_A \frac{1}{2M_A} \nabla_A^2 - \sum_i \frac{1}{2} \nabla_i^2 + \sum_{A<B} \frac{Z_A Z_B}{R_{AB}} - \sum_i \sum_A \frac{Z_A}{R_{Ai}} + \sum_{i<j} \frac{1}{r_{ij}}
\]

- Kinetic energy
- Nucleus-Nucleus attraction
- Nucleus-Electron attraction
- Electron-Electron repulsion
- Electrons-Electron repulsion (analytically unsolvable)

- Allows calculation of atomic interactions
- First Principles
- Computationally expensive, especially for finding accurate approximations of electron-electron repulsion term
Force field methods

\[ E_{\text{bond-stretch}} = \sum_{\text{1 pairs}} K_b (b - b_0)^2 \]

\[ E_{\text{bond-bend}} = \sum_{\text{angles}} K_\theta (\theta - \theta_0)^2 \]

\[ E_{\text{rotate-along-bond}} = \sum_{\text{1,4 pairs}} K_\phi \left(1 - \cos(n\phi)\right) \]

- Empirical, we need to derive values for the force field parameters (intuition, compare to experiment, compare to QM)
- MUCH faster than QM; can be applied to bigger systems
QM and FF-based approaches to reactive MD

- Option 1: Burn CPUs with QM/MD (e.g. Raty et al., PRL 2005)
- Option 2: use empirical assumptions to make QM faster (semi-empirical methods)
  - 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)
- Option 3: Add ability to simulate reactions to FF-method (empirical bond-order based force fields)
  - 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)
Classes of Models

Quantum Mechanics
- Schrödinger Eq.
- Density Functional Theory
  - Tight-Binding
    - ... 6th Order
    - 4th Order
    - 2nd Order

Classical Potentials
- Analytical
- Empirical
  - qAIREBO, ReaxFF
  - ... AIREBO
  - BOP4
  - REBO
  - BOP2
  - Tersoff

from Steve Stuart, Clemson University
How to make a force field reactive: building the ReaxFF reactive force field

- Concepts of covalent non-reactive force fields
- Introduction of bond orders
- Non-bonded interactions in a reactive force field
- Charge polarization
- Current status of the ReaxFF method
- ReaxFF program, in- and output files
Concepts of covalent non-reactive force fields

\[ E_{\text{system}} = E_{\text{bond}} + E_{\text{angle}} + E_{\text{torsion}} + E_{\text{vdWaals}} + E_{\text{Coulomb}} \]

\[ E_{\text{bond}} = k_b (r - r_o)^2 \]

\[ E_{\text{angle}} = k_v (\varphi - \varphi_o)^2 \]

\[ E_{\text{torsion}} = V_2 \cdot (1 - \cos 2\omega) + V_3 \cdot (1 + \cos 3\omega) \]

\[ E_{\text{vdWaals}} = D_{ij} \left\{ \exp \left[ \alpha_{ij} \left( 1 - \frac{r_{ij}}{r_{vdW}} \right) \right] - 2 \cdot \exp \left[ \frac{1}{2} \alpha_{ij} \left( 1 - \frac{r_{ij}}{r_{vdW}} \right) \right] \right\} \]

\[ E_{\text{Coulomb}} = C \cdot \frac{q_i \cdot q_j}{r_{ij}} \]

System energy description for a simple harmonic non-reactive force field

- 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
Failure of the harmonic model

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.
From non-reactive to reactive force fields: key features of ReaxFF

- 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.

- 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.
Introduction of bond orders

Calculation of bond orders from interatomic distances

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

$$+ \exp \left[ p_{bo,3} \cdot \left( \frac{r_{ij}}{r_o^\pi} \right)^{p_{bo,4}} \right]$$

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

Graph showing bond orders vs. interatomic distance (Å) with different bond types.
Calculation of bond energy from bond orders

\[ E_{bond} = -D_e^\sigma \cdot BO_{ij}^\sigma \cdot f(BO_{ij}^\sigma) - D_e^\pi \cdot BO_{ij}^\pi - D_e^{\pi\pi} \cdot BO_{ij}^{\pi\pi} \]
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: \(x_6 \ y_6 \ z_6\)

**Connection table**

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

**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**

**Connectivity**

**MM or MD routine**

**Fixed**
Dealing with overcoordination

Avoid unrealistically high amounts of bond orders on atoms

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

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

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

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

\[ \Delta_i = \text{Valency}_i - \sum_{j=1}^{\text{neighbours}} BO_{ij} \]
From non-reactive to reactive force fields: key features of ReaxFF

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Valence angles

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

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

\( BO_a = \text{Bond order a} \)
\( BO_b = \text{Bond order b} \)
\( \phi = \text{Angle} \)
\( \phi_o = \text{Equilibrium angle} \)
Torsion and conjugation

- Torsion angle energy term

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

- 4-body (torsion) conjugation term

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

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

- 3-body (angle) conjugation term

\[ E_{\text{con}} = p_{\text{cot1}} \cdot \frac{1}{1 + \exp(p_{\text{cot2}} \cdot \Delta_{ij}^{\text{val}})} \cdot \exp\left[-p_{\text{con3}} \cdot \left(-BO_{ij} + \sum_{n=1}^{\text{neighbours}(i)} BO_{in}\right)^2\right] \cdot \exp\left[-p_{\text{con3}} \cdot \left(-BO_{jk} + \sum_{n=1}^{\text{neighbours}(i)} BO_{kn}\right)^2\right] \cdot \exp\left[-p_{\text{con4}} \cdot (BO_{ij} - 1.5)^2\right] \cdot \exp\left[-p_{\text{con4}} \cdot (BO_{jk} - 1.5)^2\right] \]
Hydrogen bonds

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

- Bond order dependent
- Tested for a wide range of hydrogen transfer reactions
- Tested for bulk water and proton diffusion in water
- 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.

- 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.
Non-reactive force field: ignore vdWals and Coulomb interactions between atoms sharing a bond (l-j, j-k, k-l and l-m) or a valence angle (l-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

- 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 \cite{DawBaskes1984}), allowing ReaxFF to describe bulk metals

\[
E_{\text{Coulomb}} = C \cdot \frac{q_i \cdot q_j}{\left( r_{ij}^3 + \left(1/\gamma_{ij}\right)^3 \right)^{1/3}}
\]
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.
Charge polarization

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

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

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

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

\[
\sum_{i=1}^{n} q_i = 0
\]

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

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

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

- 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.
- Better scaling than QM-methods (N\log N \text{ for ReaxFF, } N^3 \text{ (at best) for QM).}
Current development status of ReaxFF

- ReaxFF combines covalent, metallic and ionic elements allowing applications all across the periodic table
- All ReaxFF descriptions use the same potential functions, enabling application to interfaces between different material types
- Code has been distributed to over 60 research groups
- Parallel ReaxFF (GRASP/Reax and USC/Reax) available

ReaxFF transferability

Some ReaxFF publications


Parallel ReaxFF: GRASP/ReaxFF

- ReaxFF is incorporated in the Grasp-framework (Aidan Thompson, Sandia) allowing parallel ReaxFF-simulations.

GRASP Performance on BG/L with ReaxFF
Comparison with Liberty Cluster (3GHz Pentium+Myrinet)

RDX Explosive with Oxygen
ReaxFF force field with charge equilibration

- ReaxFF enables reactive modelling
- Si/SiO$_2$, Explosives, film growth
- Each process computes energy and forces for a virtual non-periodic cluster
- Low communication, duplicated computation $\sim P(N/P)^{2/3}$
- Uses Van Duin's Fortran subroutines for force calculation.
- Good strong scaling
- Sweet spot: 5000 atoms/processor
ReaxFF program, in- and output files

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
Overview ReaxFF in- and output files

Mandatory input files

- geo (input geometry)
- control (run control parameters)
- ffield (force field parameters)
- exe (UNIX-script)
Force field development for Si/SiO systems

- 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)
Bond energy

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

HO-Si(OH)$_3$ bond
Valence angle bending
1. Individual valence angles

H₃Si-SiH₂-OH angle

Other SiOH angles:
- Si-Si-Si
- Si-Si-H
- Si-O-Si
- H-Si-H
- Si-Si-H
- H-O-H
- Si-O-H
- O-O-O
- O-Si-H
- Si-O-O
- O-O-H
Valence angle bending
2. Ring deformation

Energy (kcal/mol)

$r_1$ (Angstrom)

DFT
ReaxFF
Valence angle bending
3. Ring size/ring strain

ΔE/SiO₂ (kcal/mol)

Monomer  4-ring  6-ring  8-ring  10-ring  12-ring  14-ring  alfa-Quartz
Over/undercoordination

\[
\begin{align*}
\text{Si(OH)}_4 + \text{HO-OH} & \rightarrow \text{Si(OH)}_6 & \Delta E (\text{DFT}) & = +60.9 \text{ kcal/mol} & \Delta E (\text{ReaxFF}) & = +48.2 \text{ kcal/mol} \\
\text{H}_3\text{Si-O-SiH}_3 + \text{H}_3\text{Si-SiH}_3 & \rightarrow \text{O(SiH}_3)_4 & & +102.5 \text{ kcal/mol} & & +87.4 \text{ kcal/mol} \\
\end{align*}
\]
Reactions

1. $\text{H}_2\text{Si}=\text{O} + \text{H}_2\text{Si}=\text{O} \rightarrow 4$-ring

![Graph showing the relationship between Si-Si distance (Å) and Energy (kcal/mol)]
Reactions

2. H₂O⁻ incorporation in a Si-cluster

- Reactive force field can be used to simulate the entire reaction pathway
The document discusses the equations of state for crystals, with a focus on All-Si crystals. The text explains how the force field recognizes a high-pressure transition from 4-coordinated (α) to 6-coordinated (β) phase.

The graphs illustrate the energy per Si atom (eV) as a function of volume per Si atom (Å³) for ReaxFF and QC models. The graphs show distinct curves for different crystal structures, labeled as Si(a), Si(b), and Si(sc), demonstrating the energy behavior across different volumes.
Compression/expansion crystals
2. Silicon oxide crystals

- ReaxFF reproduces the QC-data for both the clusters as well as the condensed phases.
Correcting a ‘finished’ ReaxFF force field

- Original ReaxFF overstabilizes 5-coordination for silicon bulk phase

MD-anneal run on bulk phase Si-α with original ReaxFF
Re-optimize ReaxFF with equation of state for 5-coordinate Si-phase

- Re-optimized ReaxFF gets proper stability for 5-coordinate Si-phase
- 5-coordinate phase is more stable than 6-coordinate Si(β)!
- 5-coordinate Si might be important in amorphous Si
MD-anneal run on bulk phase Si-α with ReaxFF
Applications of the Reax Si/SiO force field

- Hydrogen diffusion in Si/SiO$_2$ interfaces
- Stability of PDMS polymers
ReaxFF simulations on H-diffusion and bonding in $\alpha$-quartz

Hydrogen radical in 72-atom $\alpha$-quartz
T=100K; reaction enforce by a moving restraint

Seqquest:
$$E(\text{quartz}_H)-E(\text{quartz}+H)= +24 \text{ kcal/mol}$$

-Good agreement between Reax and SeqQuest reaction energies
ReaxFF simulations on H-radical diffusion through α-quartz

T=600K

32 H-radicals in 576-atom α-quartz system

No reaction of H-radicals with lattice oxygens; all H-radicals diffuse and form H₂
ReaxFF simulations on H-radical diffusion through $\alpha$-quartz

$T=1000K$

32 H-radicals in 576-atom $\alpha$-quartz system

-Elevated temperatures result in H-reaction with lattice oxygens. H$_2$ formation still dominates
Conclusions

- ReaxFF has proven to be transferable to a wide range of materials and can handle both complex chemistry and chemical diversity. Specifically, ReaxFF can describe covalent, metallic and ionic materials and interactions between these material types.

- The low computational cost of ReaxFF (compared to QM) makes the method suitable for simulating reaction dynamics for large (>> 1000 atoms) systems (single processor). ReaxFF has now been parallelized, allowing reactive simulations on >>1000,000 atoms.