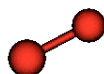
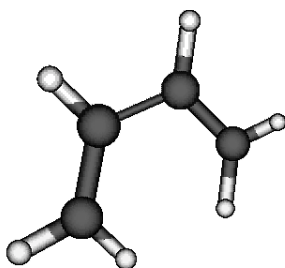


Development of the ReaxFF reactive force fields and applications to combustion

Adri van Duin

Associate Professor

Department of Mechanical and Nuclear Engineering
Pennsylvania State University, 136 Research East Building
phone: 814-8636277; E-mail acv13@psu.edu

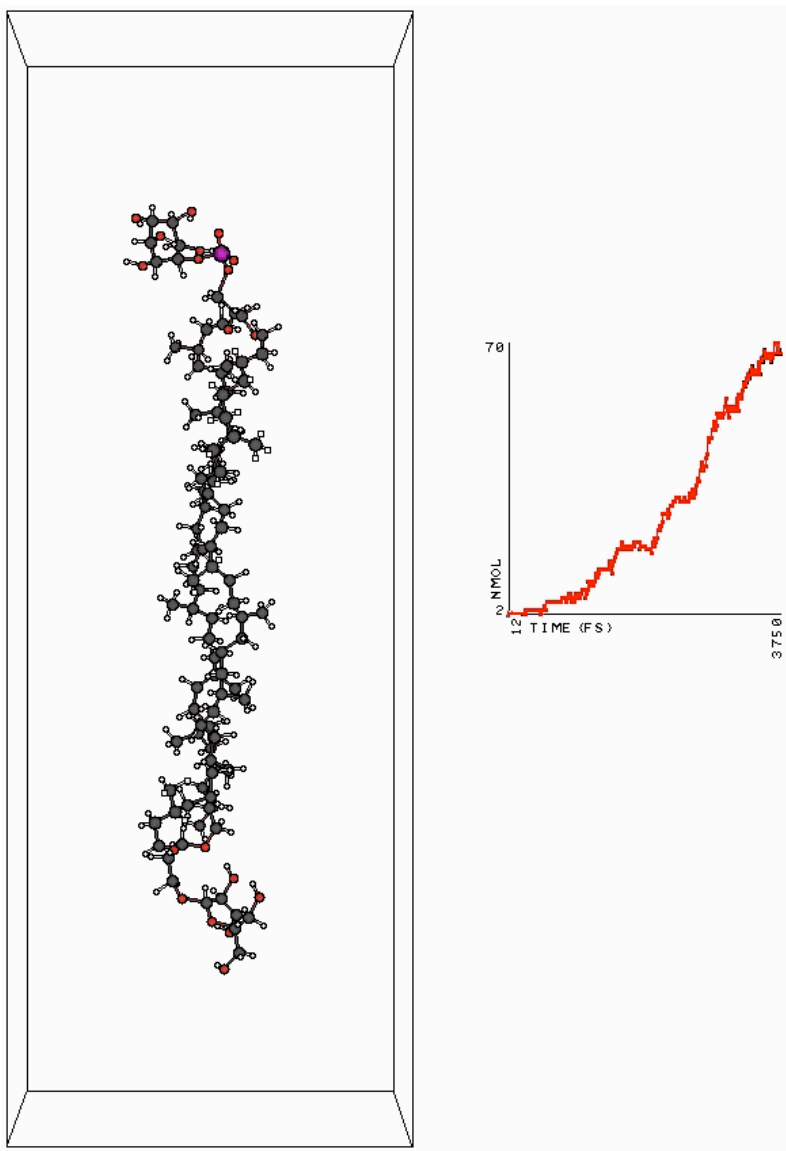


ReaxFF pathway for butadiene oxidation

TMB-2009



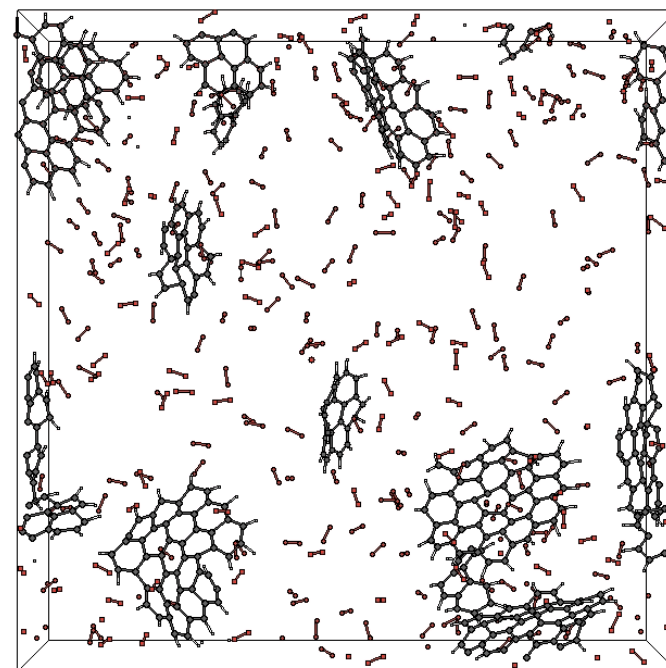
Aim: simulation of the dynamics of large, complicated reactive systems



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

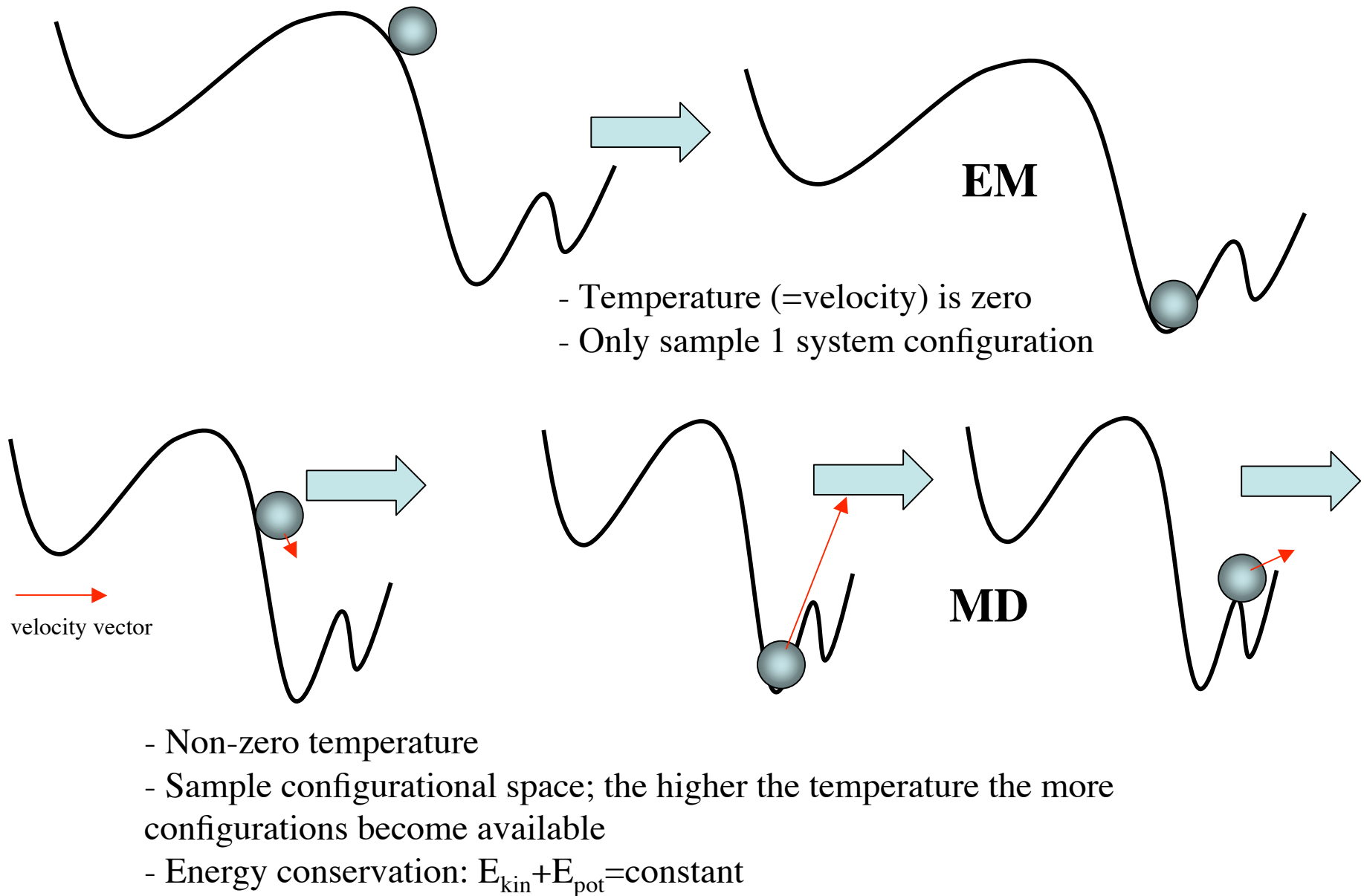
Outline

- 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
- Applications to combustion chemistry
- Applications to surface catalysis

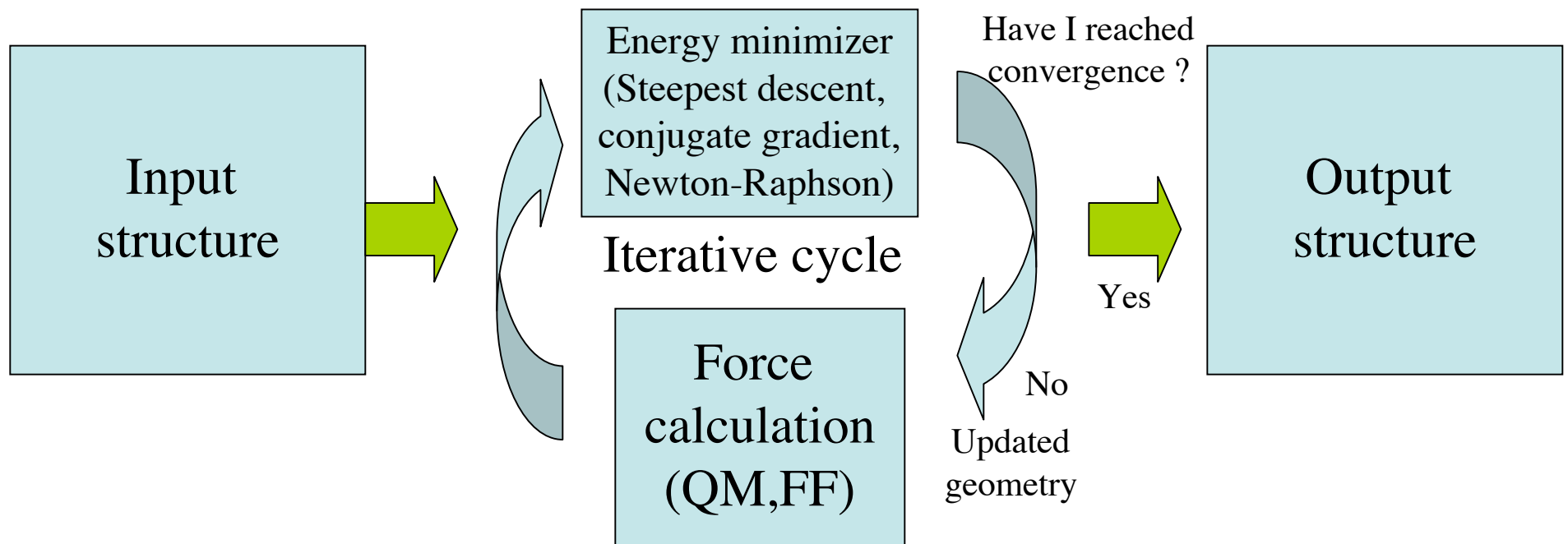


ReaxFF simulation of char combustion
(collaboration with Jonathan Matthews)

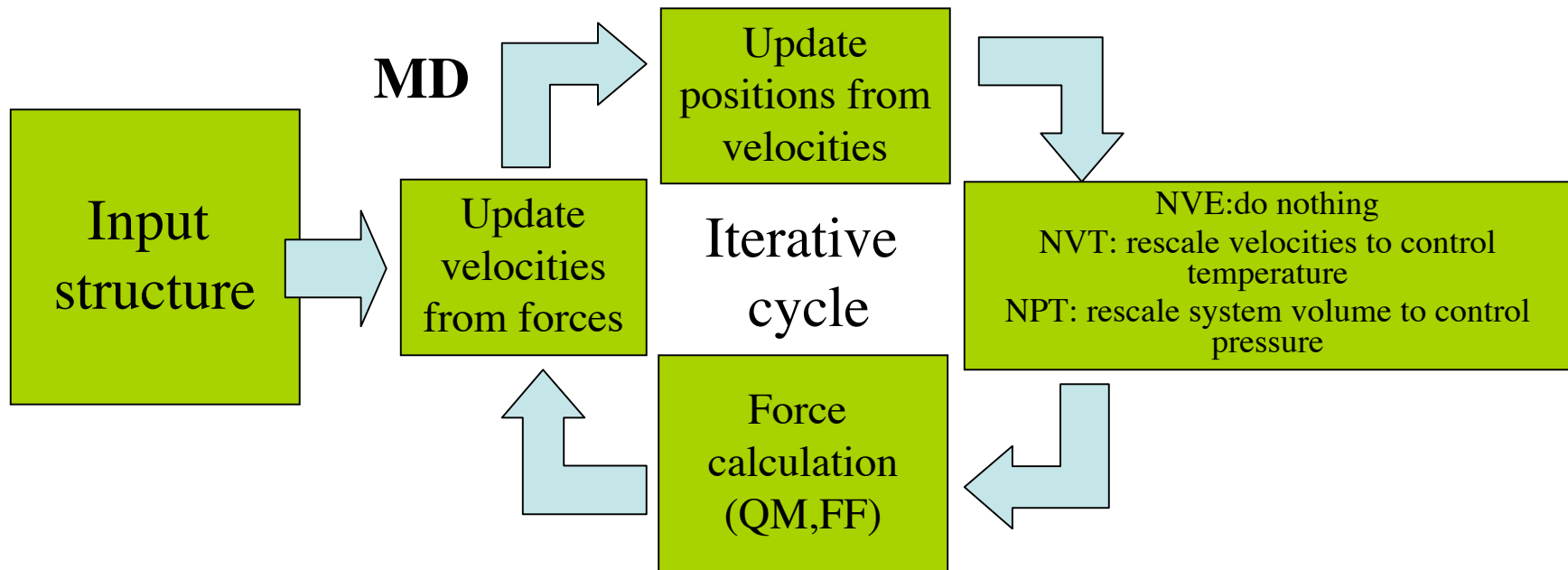
Energy minimization (EM) and molecular dynamics (MD) methods

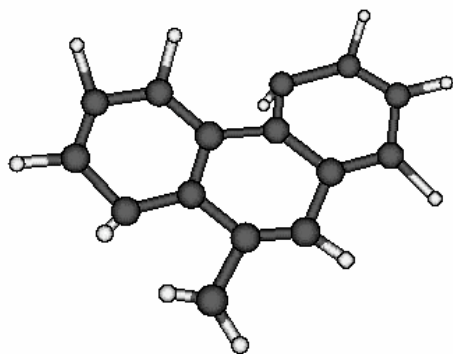


Energy minimization methods: structure



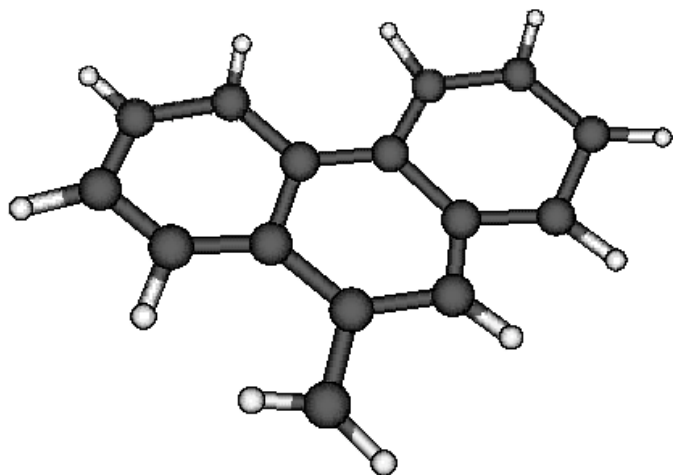
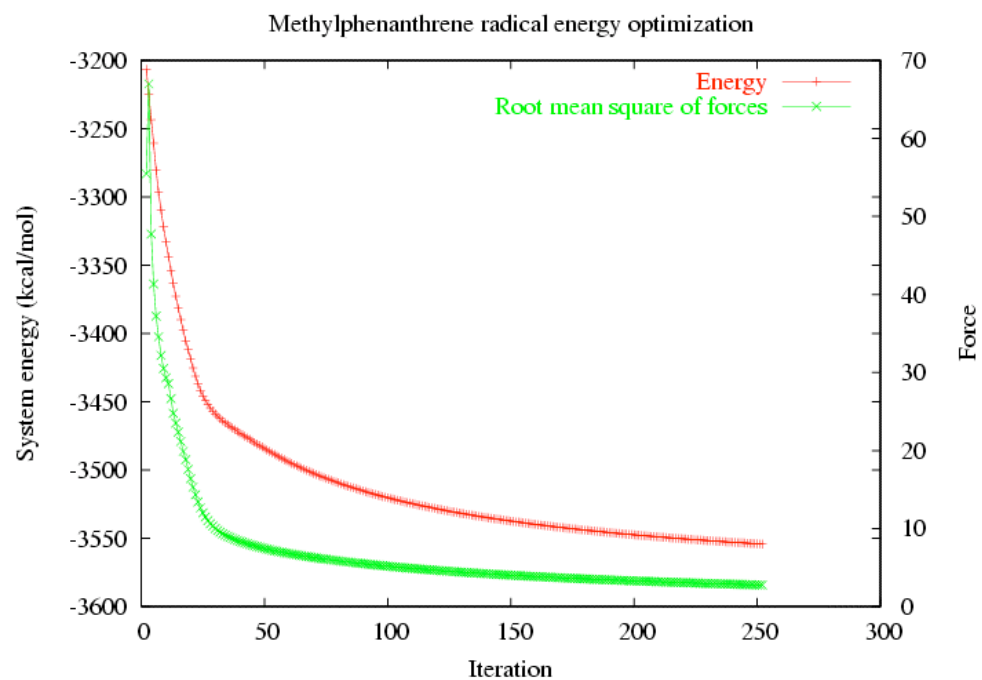
MD-methods: structure





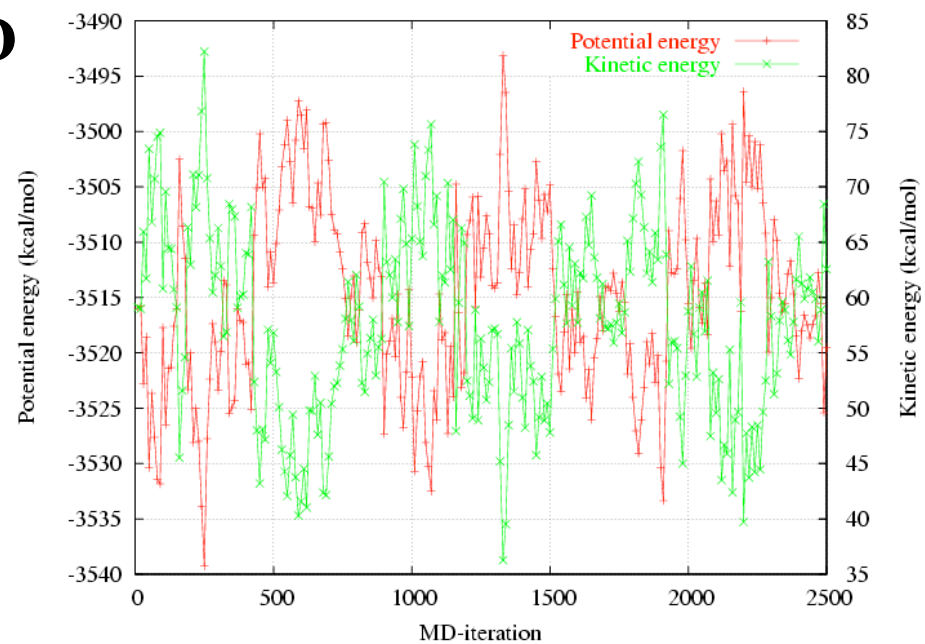
FF energy minimization of a methylphenanthrene radical using a steepest descent method

EM



FF NVE molecular dynamics of a methylphenanthrene radical at T=700K

MD



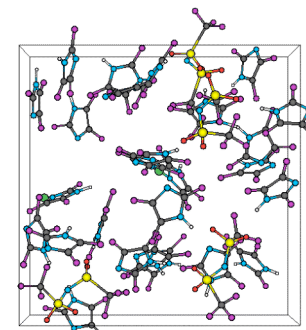
Applications of EM and MD

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.

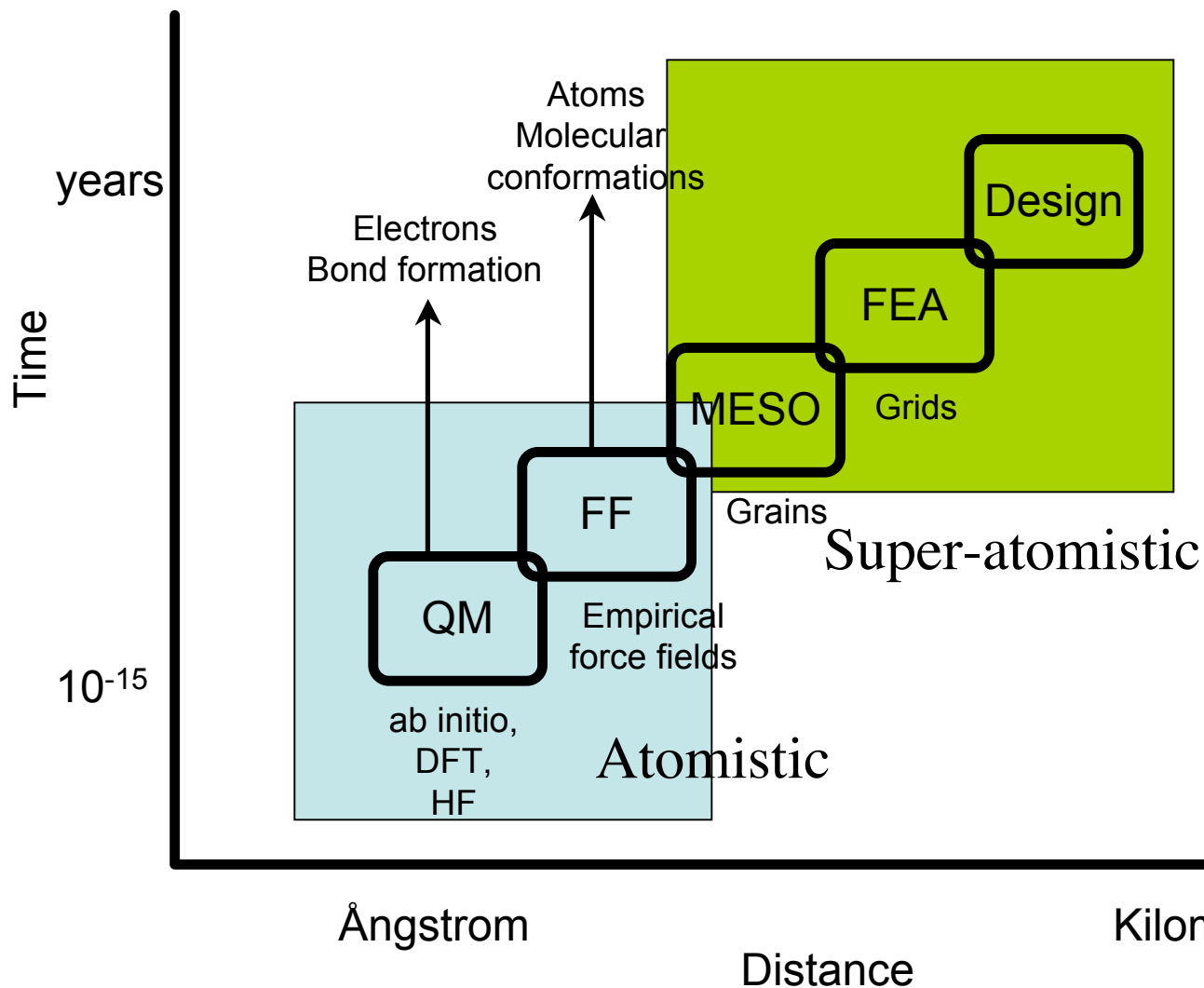
MD

- 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



Fluorimidazole
/HTFS system

Simulations on the dynamics of chemical reactions



QM methods:

- Fundamental
- Expensive, only small systems

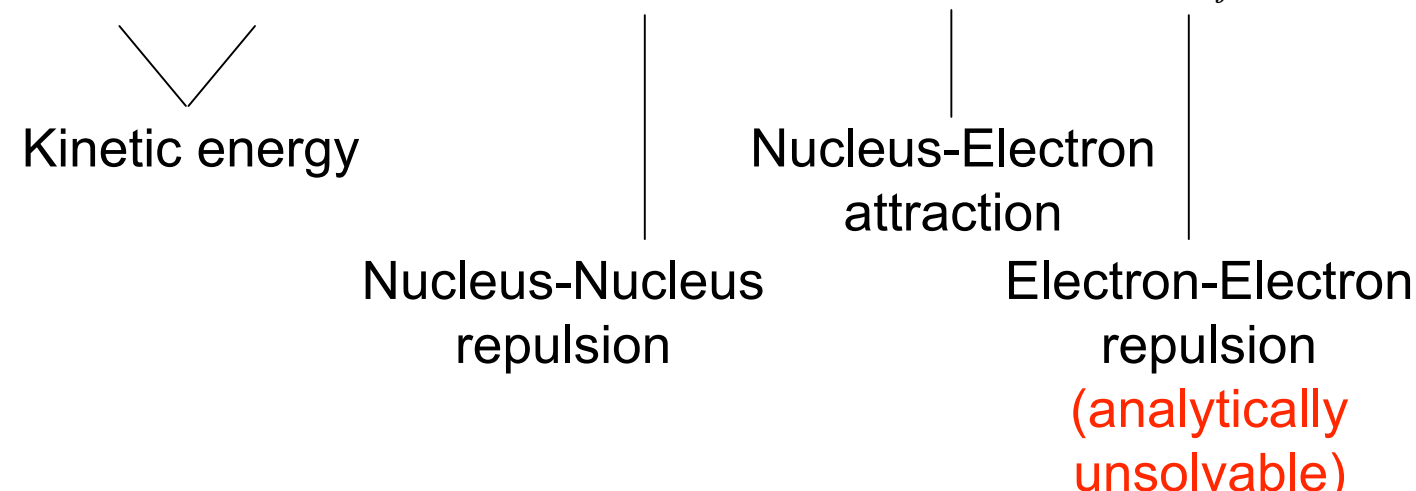
FF methods

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

QM-methods

$$\mathbf{H}\Psi = E\Psi$$

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



Kinetic energy

Nucleus-Nucleus repulsion

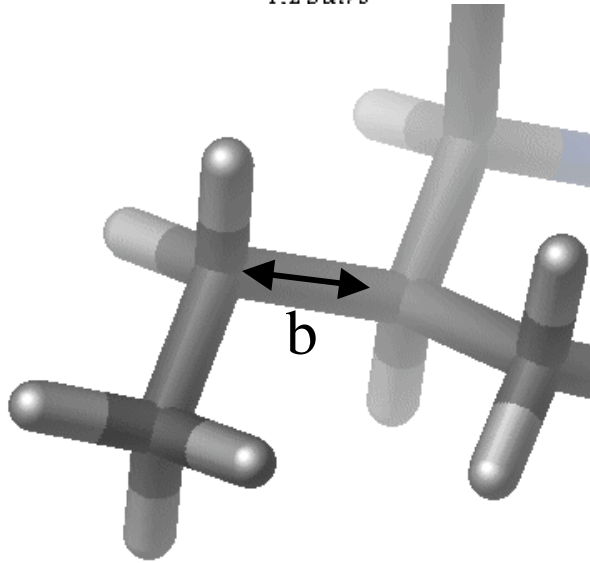
Nucleus-Electron attraction

Electron-Electron repulsion
(analytically unsolvable)

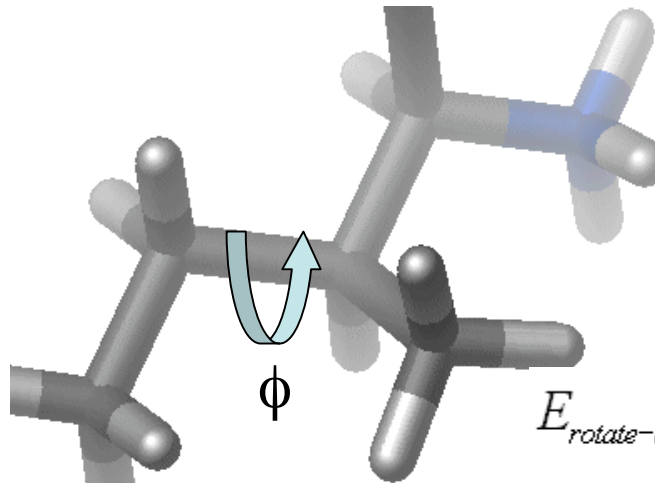
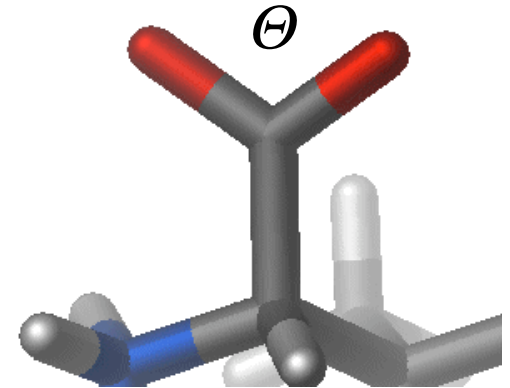
- Allows calculation of atomic interactions First Principles
- Computationally expensive, especially for finding accurate approximations of electron-electron repulsion term

Force field methods

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



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

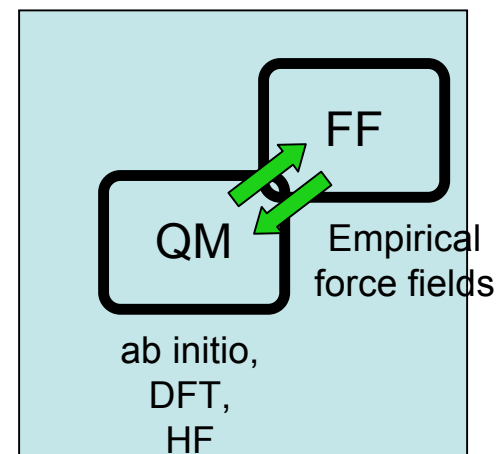


$$E_{\text{rotate-along-bond}} = \sum_{1,4 \text{ pairs}} K_\phi (1 - \cos(n\phi))$$

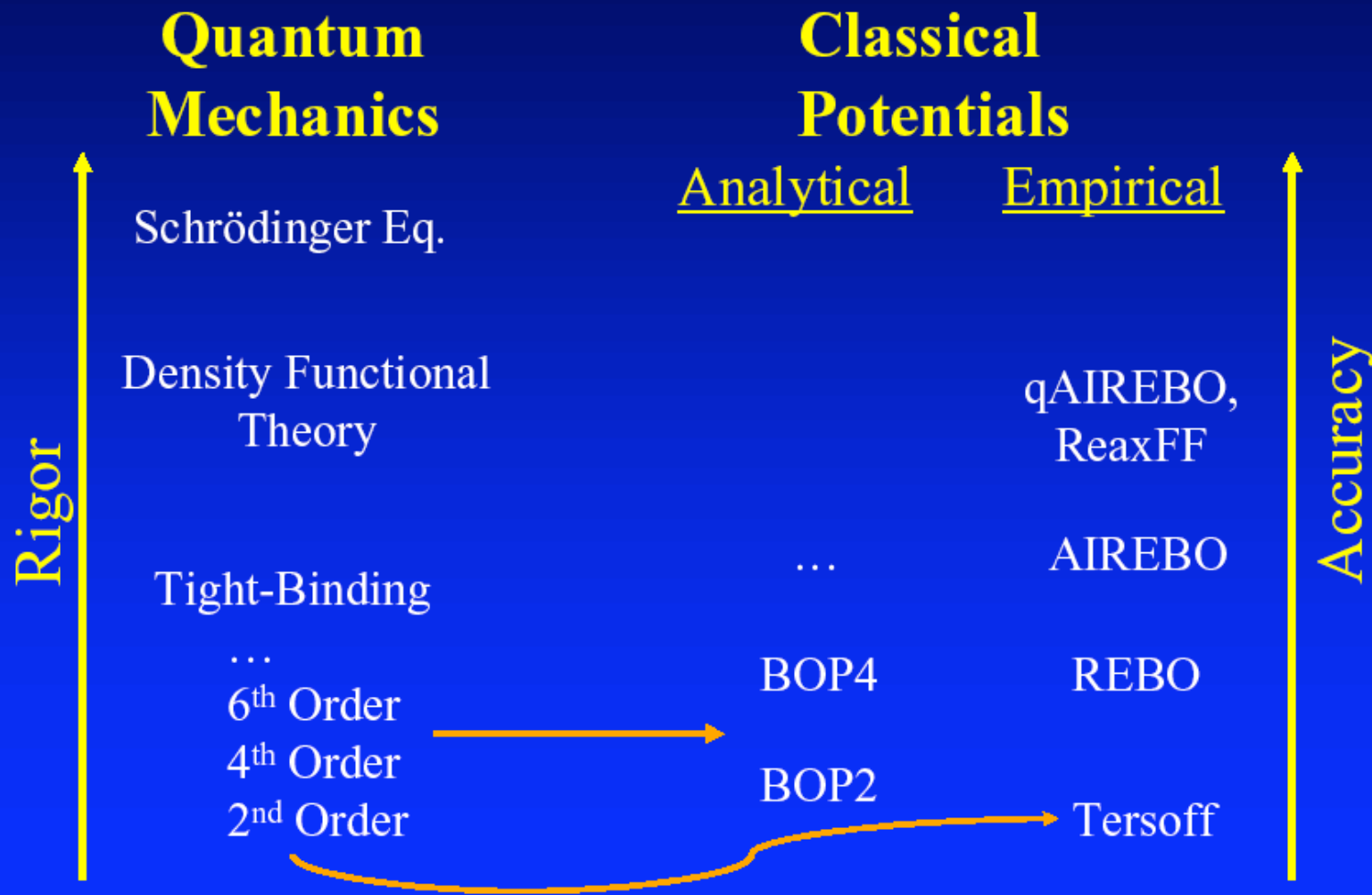
- Empirical, we need to derive values for the force field parameters (intuition, compare to experiment, compare to QM)
- MUCH faster than QM; can be applied to bigger systems

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)
 - 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)



Classes of Models



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

Concepts of covalent non-reactive force fields

$$E_{system} = E_{bond} + E_{angle} + E_{torsion} + E_{vdWaals} + E_{Coulomb}$$

$$E_{bond} = k_b (r - r_o)^2$$

$$E_{angle} = k_v (\varphi - \varphi_o)^2$$

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

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

$$E_{Coulomb} = C \cdot \frac{q_i \cdot q_j}{r_{ij}}$$

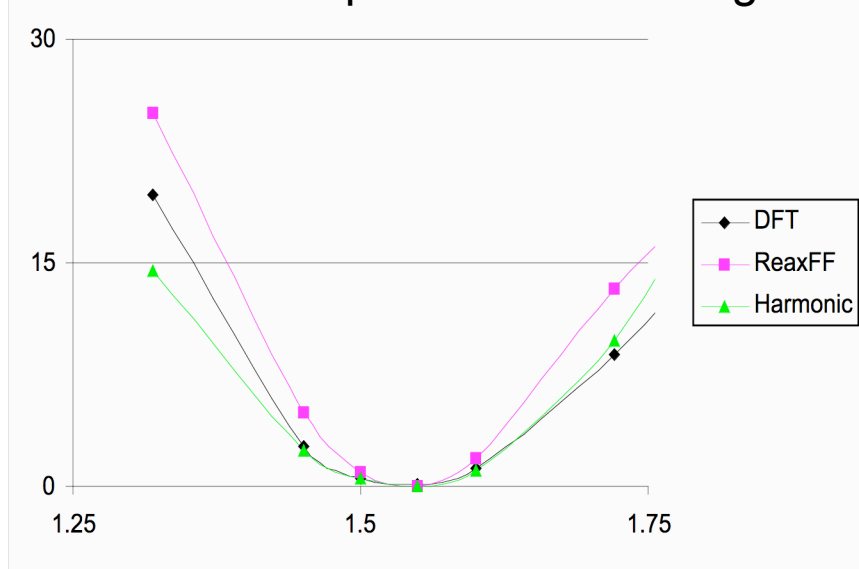
- Can be parameterized to describe structures and energies close to equilibrium
- Expansion with anharmonic terms improves reliability and application range
- Does not dissociate bonds properly

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

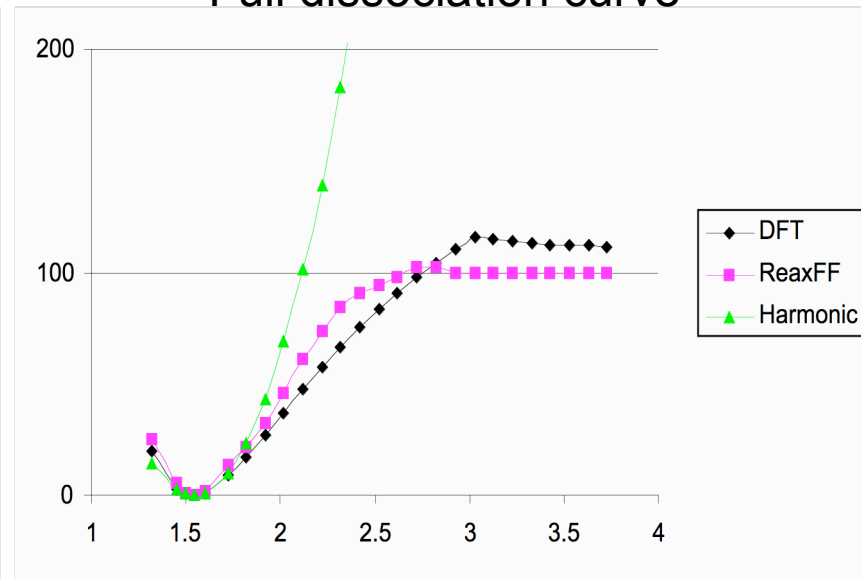
Failure of the harmonic model

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.

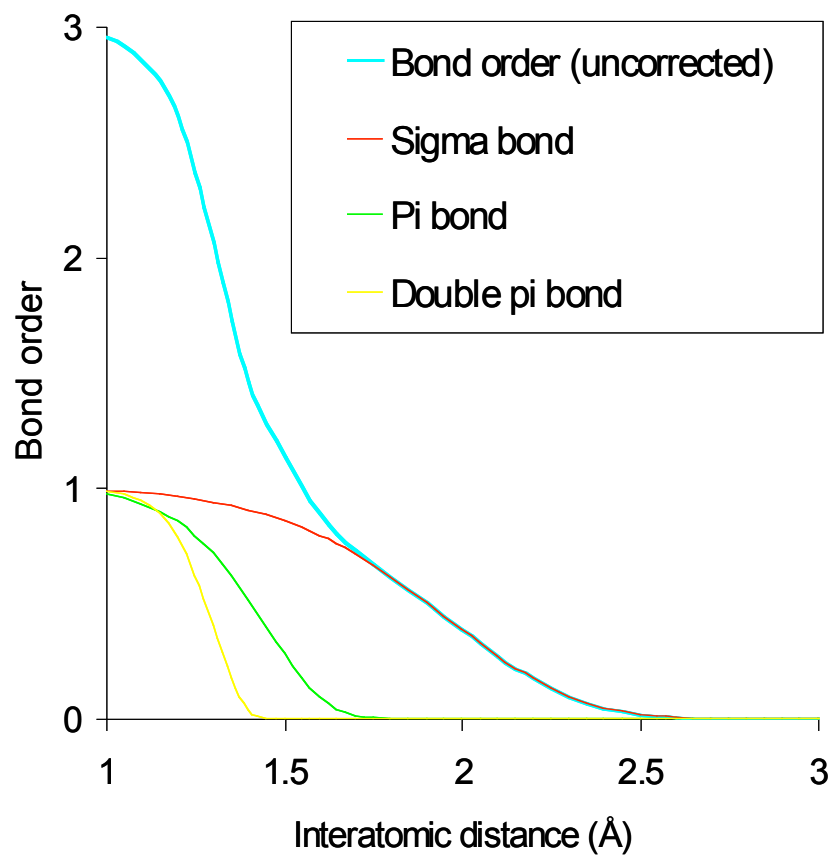
- Nonbonded interactions (van der Waals, Coulomb) are calculated between **every** atom pair, irrespective of connectivity. Excessive close-range nonbonded interactions are avoided by shielding.

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

Introduction of bond orders

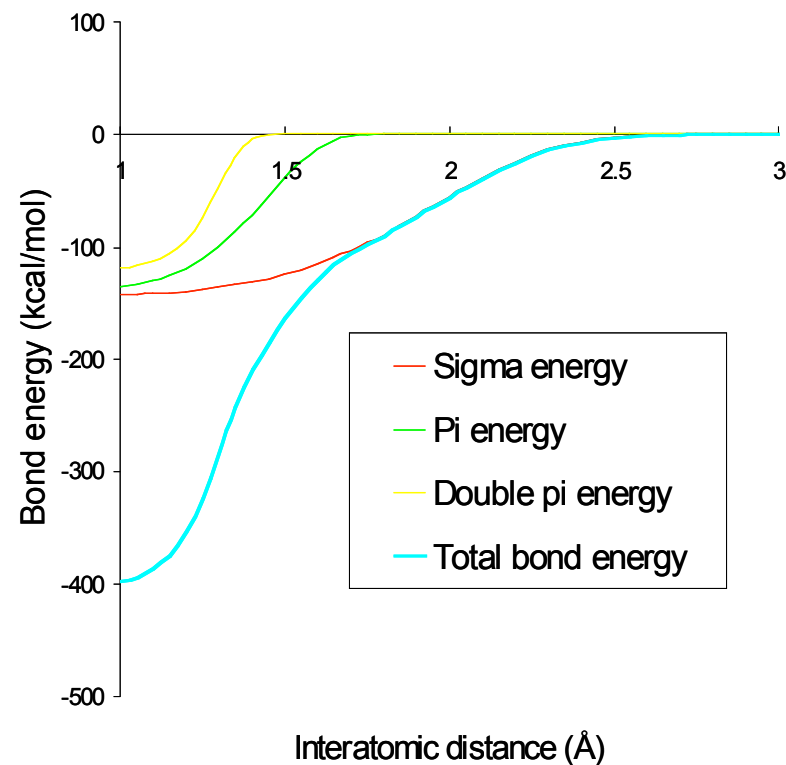
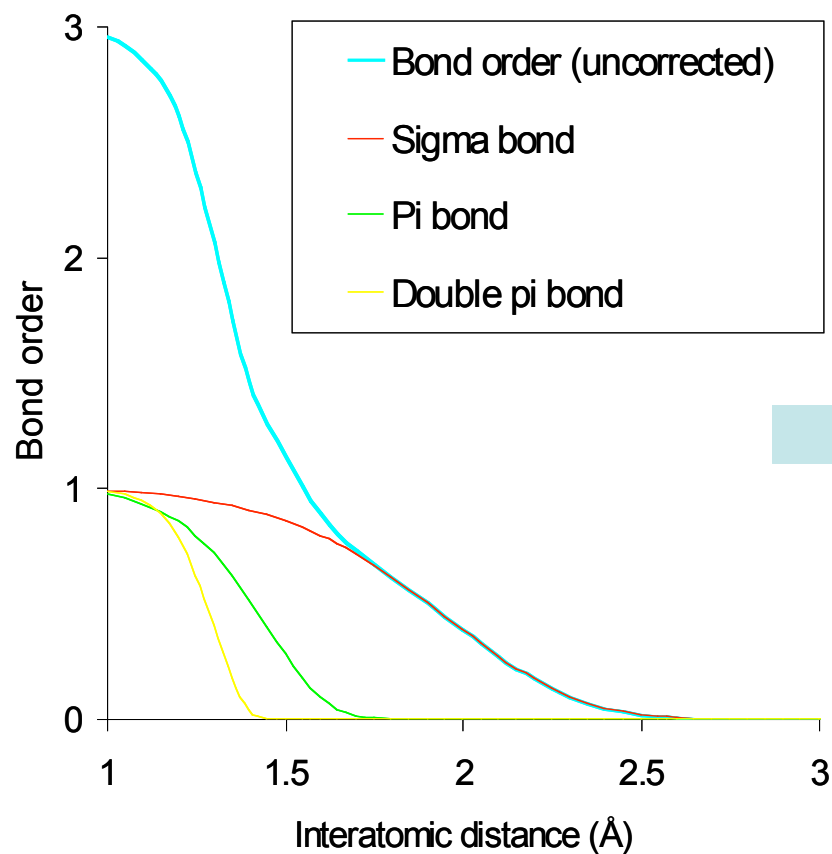
Calculation of bond orders from interatomic distances

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



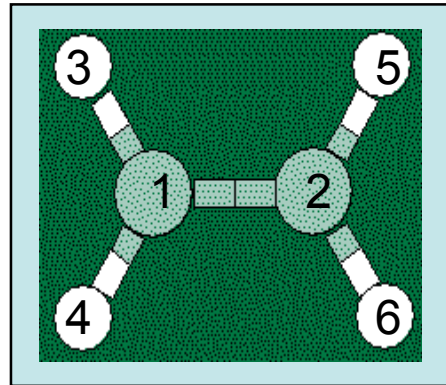
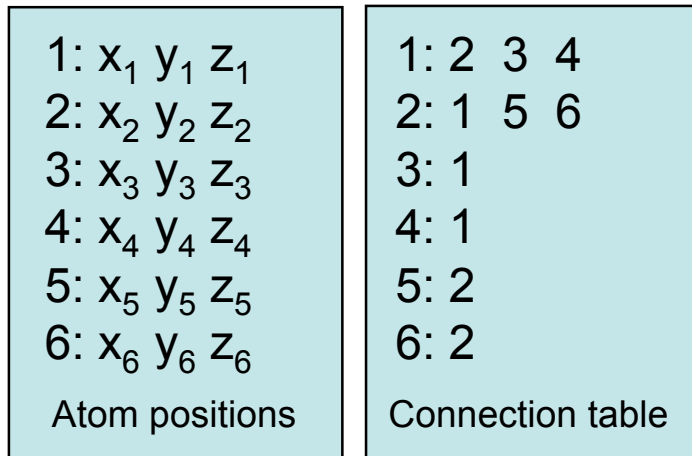
Calculation of bond energy from bond orders

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

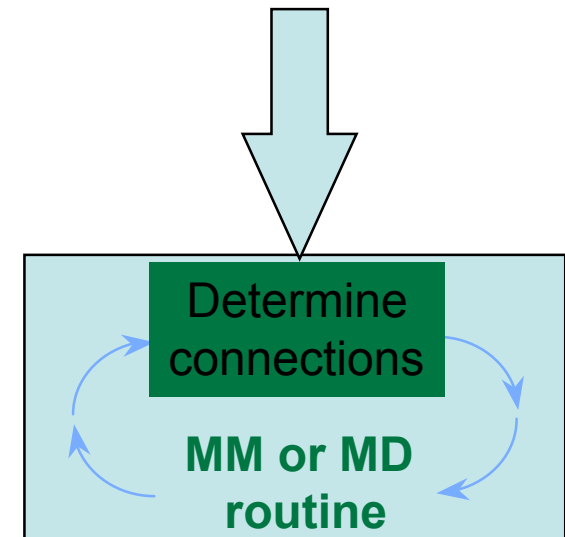
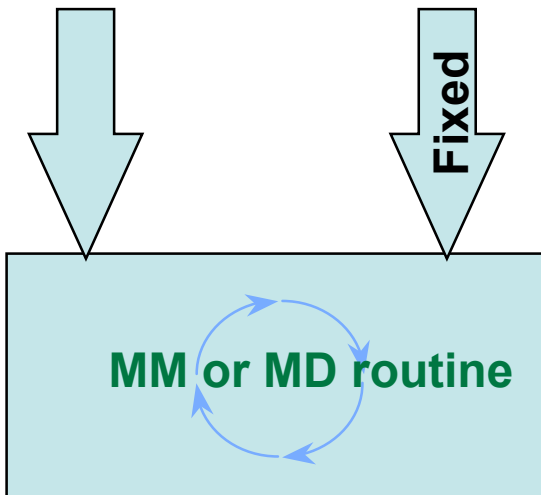
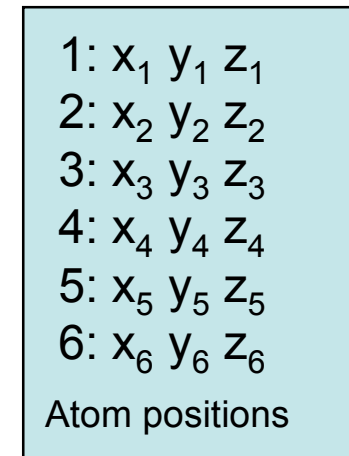


Connectivity: differences in program structure

Non-reactive force field

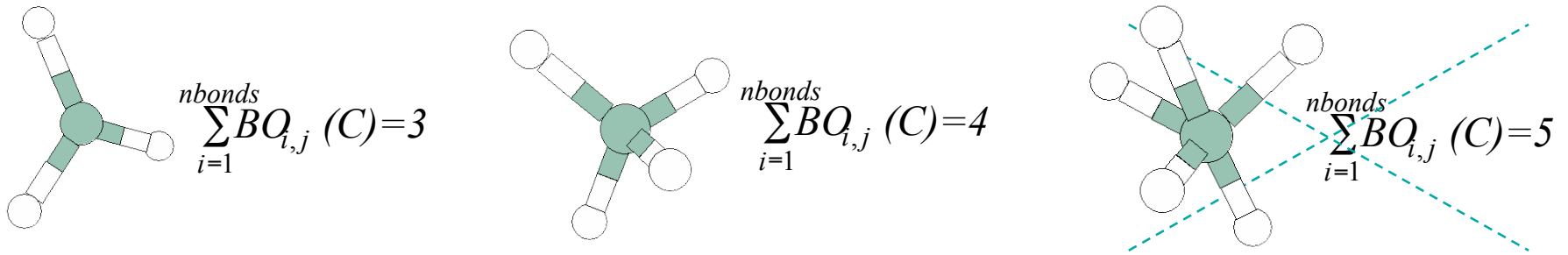


Reactive force field



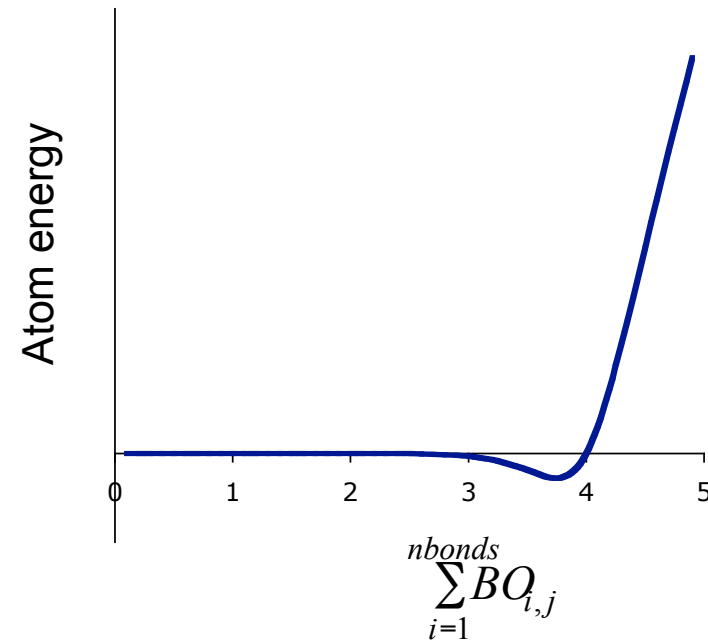
Dealing with overcoordination

Avoid unrealistically high amounts of bond orders on atoms



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

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



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

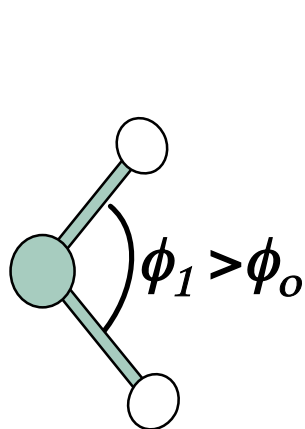
-To get a smooth transition from nonbonded to single, double and triple bonded systems ReaxFF employs a bond length/bond order relationship. Bond orders are updated every iteration.

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

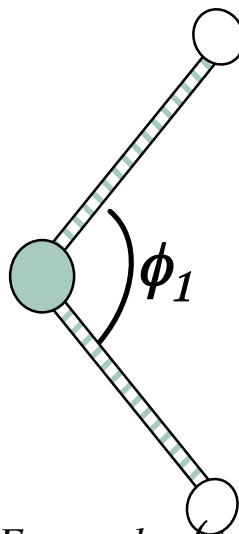
- Nonbonded interactions (van der Waals, Coulomb) are calculated between **every** atom pair, irrespective of connectivity. Excessive close-range nonbonded interactions are avoided by shielding.

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

Valence angles

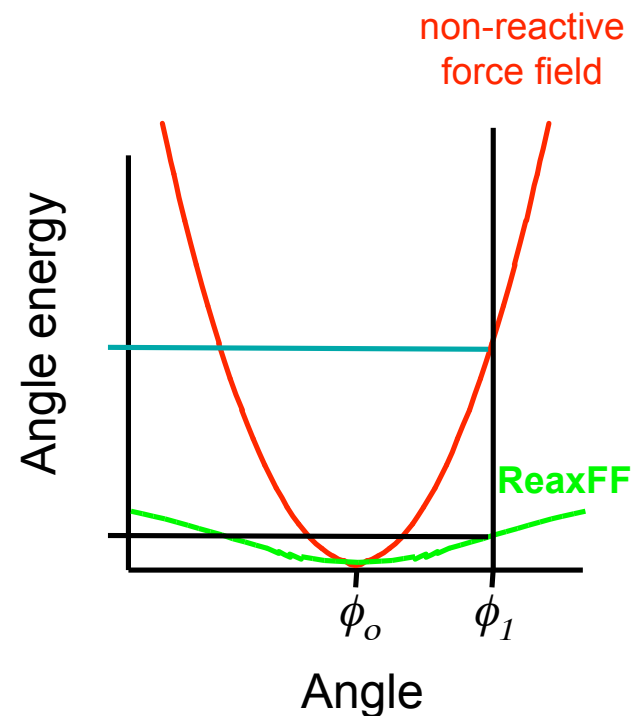


Bond orders: 1



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

Bond orders: 0.4



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

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

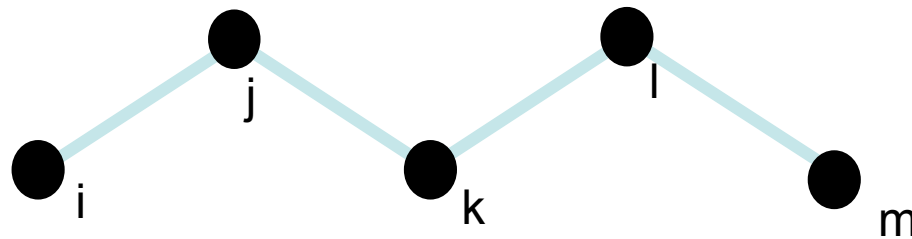
Bond-order dependent part

BO_a = Bond order a
 BO_b = Bond order b
 ϕ = Angle
 ϕ_o = Equilibrium angle

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.
- 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.

Nonbonded interactions



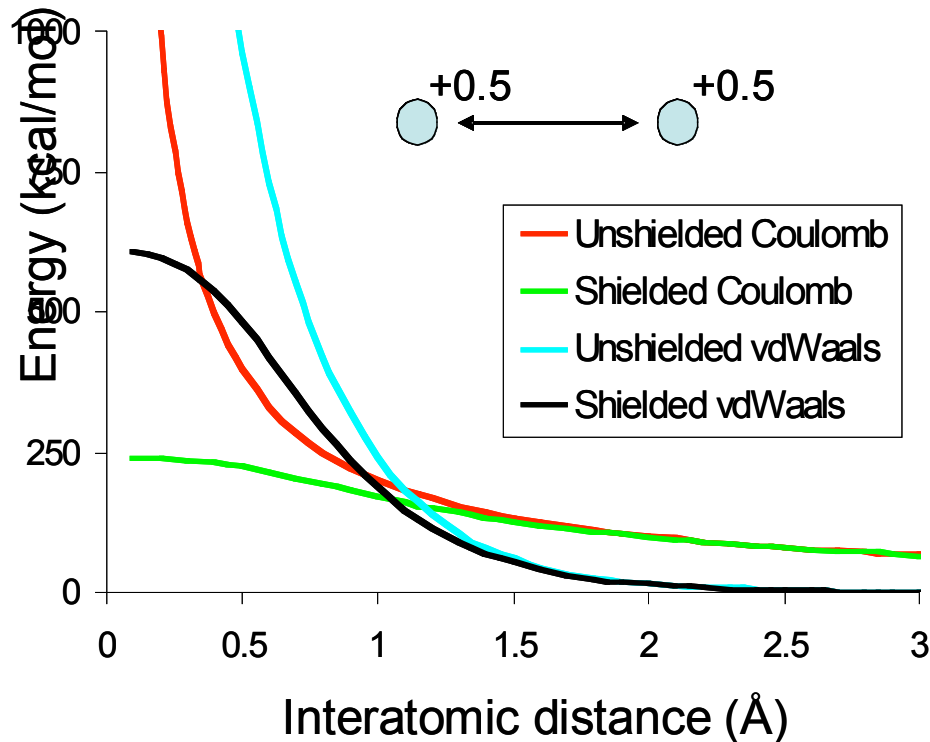
Non-reactive force field: ignore vdWaals and Coulomb interactions between atoms sharing a bond (i-j, j-k, k-l and l-m) or a valence angle (i-k, j-l and k-m).

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 vdWaaals 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

vdWaaals: Shielded Morse potential

- For metals ReaxFF only uses bond energy, overcoordination, vdWaaals and Coulomb-terms (no angle or dihedrals)
- vdWaaals and overcoordination terms serve as a density-dependent repulsive term (as used in EAM-potentials [Daw and Baskes, PRB 1984]), allowing ReaxFF to describe bulk metals

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

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

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

.....

.....

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

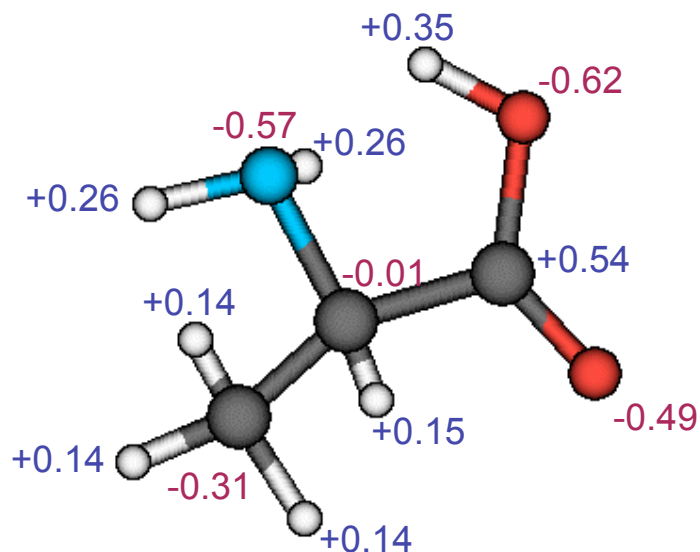
$$\sum_{i=1}^n q_i = 0$$

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

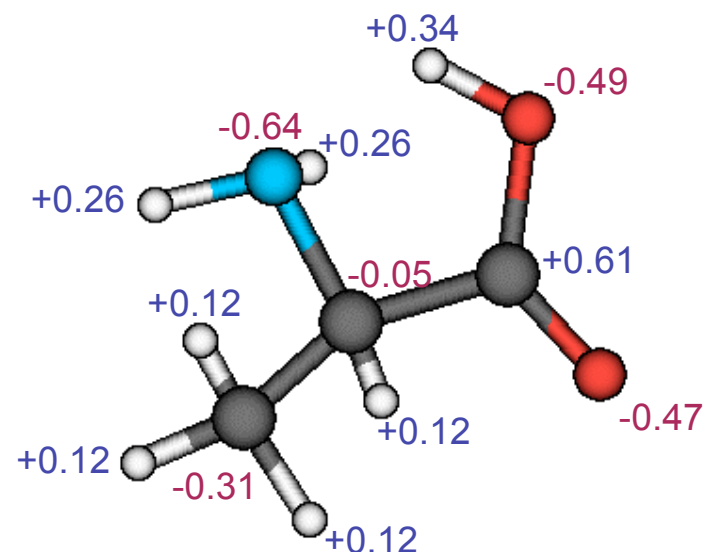
Similar to Qeq-method
(Rappe and Goddard, J.
Phys. Chem. 1991) with
empirical shielding
correction.

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

ReaxFF charges



QM
Mulliken charges
DFT; 6-31G**

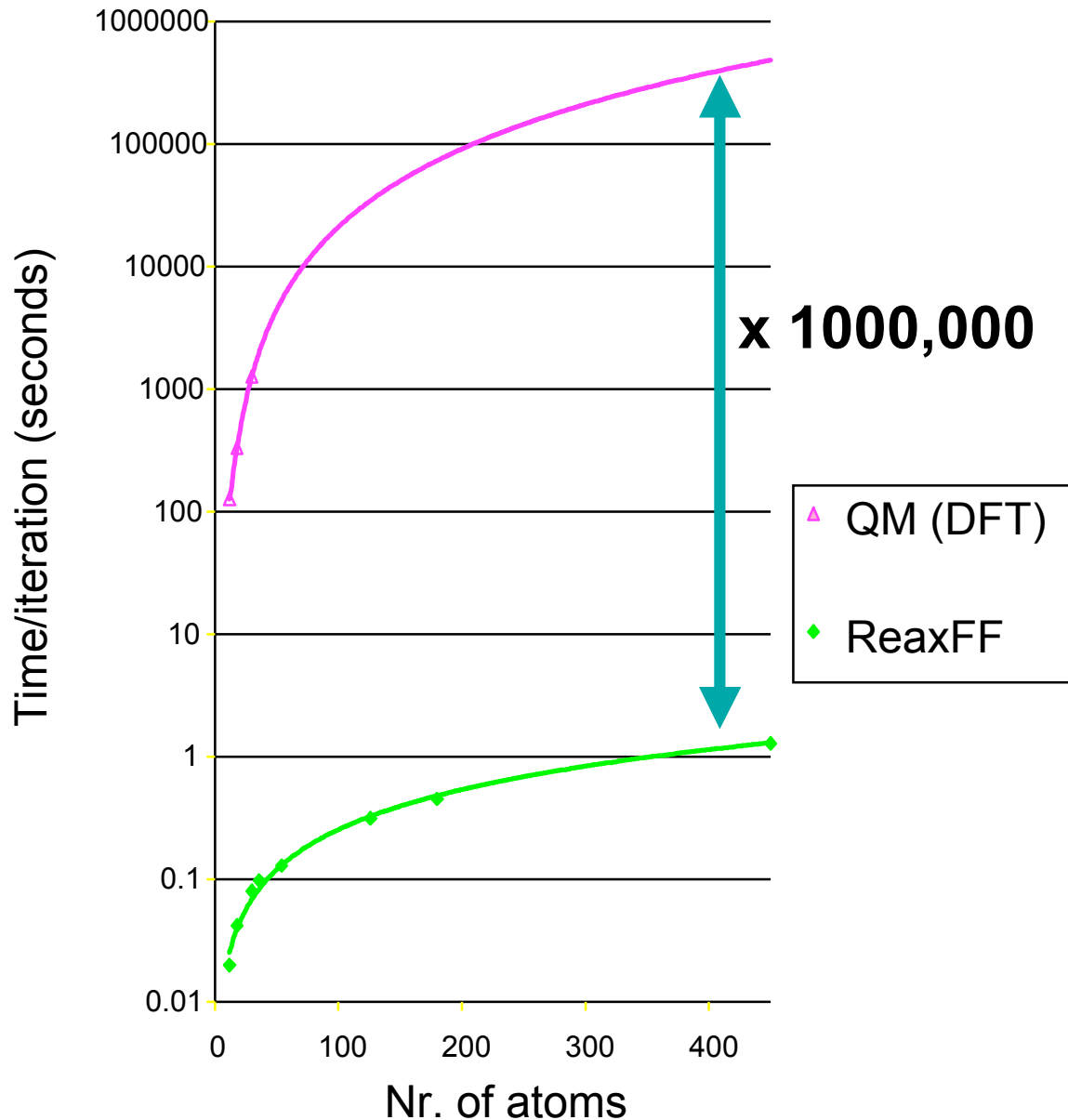


- Good reproduction of Mulliken charges (similar concepts)
- Combined with 1-2 Coulomb-interactions, this enables ReaxFF to simulate polarization effects on local chemistry
- EEM/Qeq methods work well around equilibrium; incorrect description of charge flow at high compression and dissociation (Chen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

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 ($N\log N$ for ReaxFF, N^3 (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

Legend:

- alkali metals
- alkaline earth metals
- transition metals
- other metals
- other nonmetals
- halogens
- noble gases
- lanthanides
- actinides

not currently described by ReaxFF

Some ReaxFF publications

- C/H: van Duin et al, JPC-A 2001, 105, 9396; Org. Geochem. 2003, 34, 515; Chen et al, PR-B 2005, 72, 085416, Han et al. Appl. Phys. Lett. 2005, 86, 203108.
- C/N/O/H: Strachan et al, PRL 2003, 91, 09301; JCP 2005, 122, 054502; van Duin et al, JACS 2005, 127, 11053
- Metals: Zhang et al, PRB 2004, 69, 045423; Nielson et al., JPC-A 2005, 109, 493; Su et al., PRB 75, 2007; Ludwig et al, JPC-B 2006; Cheung et al, JPC-A 2005, 109, 851
- Si/SiO/SiC: van Duin et al., JPC-A 2003, 107, 3803; Chenoweth et al., JACS 2005, 127, 7192; Buehler et al., PRL 2006, 96, 095505; Buehler et al, PRL 2007.

ReaxFF users September 16 2006.

Name	Institute	Distribution date	Application
Aidan Thompson	Sandia National Lab	July 2005	Incorporation into GRASP
Ioana Cozmuta	NASA/AMES	May 2006	N/O impact on ceramics
Anatoly Beloshenko	U. Uppsala, Sweden	February 2006	H ₂ /D ₂ shock
Ara Kooser	Sandia National Labs	February 2005	Si/SiO ₂
Ashwin R'maniam	Caltech	April 2006	Mo dislocations
Blas Pedro Uberuga	Los Alamos National Lab	June 2004	PAH-clusters
Angela Violi	U. Utah	April 2003	PAH-clusters
Eduardo Bringa	Livermore National Labs	May 2006	Li/C/H systems
Elodie Salmon	IFP, France	February 2006	Kerogen cracking
Erik Santiso	NC State U.	February 2004	Hydrocarbons
R.J.M. Konings	Inst.for TransU, Germany	May 2006	Uraniumnitride
Florent Calvo	Lab. Phys.Quant. France	August 2005	Si/SiO clusters
Gyeong Hwang	U. Austin	October 2005	Si/SiO suboxides
Halvor Hanssen	U. Trondheim, Norway	February 2006	Cellulose
Timo Jacob	FHI Berlin, Germany	January 2004	Ru/Se alloys, QM/MM
Jay Quenneville	Los Alamos National Lab.	February 2006	High-energy materials
Jeff Ludwig	U. Delaware	December 2005	Pt surfaces with H ₂
Jeremy Kua	U. San Diego	April 2006	SbCl, Borides
Jean-Bernard Maillet	CEA, France	January 2004	High-energy materials
Kai Nordlund	U. Helsinki, Finland	June 2006	Nanotubes/gold
Lingti Kong	U. Montreal, Canada	July 2006	Si/SiO ₂
Micael Baudin	U. Uppsala, Sweden	October 2005	Zn/ZnO
Nicholas Winter	Livermore National Lab.	August 2004	High-energy materials
Paul Mikulski	US Naval Academy	May 2005	Amorphous carbon
Poonam Doiphode	Inst. for Plasma Res. India	February 2005	Hydrocarbons
Renee van Ginhoven	Sandia National Labs.	February 2005	Si/SiO ₂ interfaces
Rob Riggelman	U. Madison	August 2004	Organosilicates
Markus Buehler	MIT	August 2005	Crack propagation
Rick Muller	Sandia National Labs.	January 2004	Software development
Sangsoo Han	KAIST, Korea	January 2004	Li/C/H/B force fields
Scott Dunham	U. Washington	August 2003	Hydrocarbons, Si/SiO ₂
Sergio Calvo	Texas A&M	March 2005	Pt/H/O catalysis
Philippe Simonetti	CEA, France	February 2004	Hydrocarbons, C-F
Sofia Akber	Scripps Institute	February 2006	High-pressure iron
Sonia Tulyani	U. Massachusetts	March 2006	Hydrocarbons
Tim Germann	Los Alamos National Labs.	November 2004	Software development
Per-Olof Astrand	U. Trondheim, Norway	December 2005	Pt/C, proteins, water
Priya Vashishta	USC	November 2005	Software development
Greg Voth	U. Utah	February 2004	PAH-clusters
Victor Vasquez	U. Nevada	June 2005	Hydrazine
Wolfgang Bessler	U. Heidelberg, Germany	March 2006	Fuel cells
Yehuda Zeiri	Hebrew U., Israel	November 2004	IED
Zhitao Xu	U. Calgary	December 2005	Proteins, organophosphates
Alejandro Strachan	Purdue U.	August 2005	Ferroelectrics
Tahir Cagin	TexasA&M	January 2006	High-energy materials
Julius Ojwang'	TU Eindhoven Holland	April 2006	Alanates

ReaxFF user community



Parallel ReaxFF: GRASP/ReaxFF

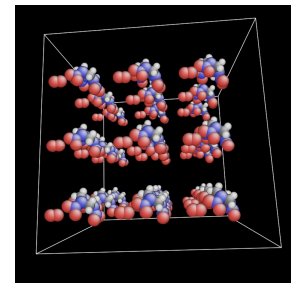
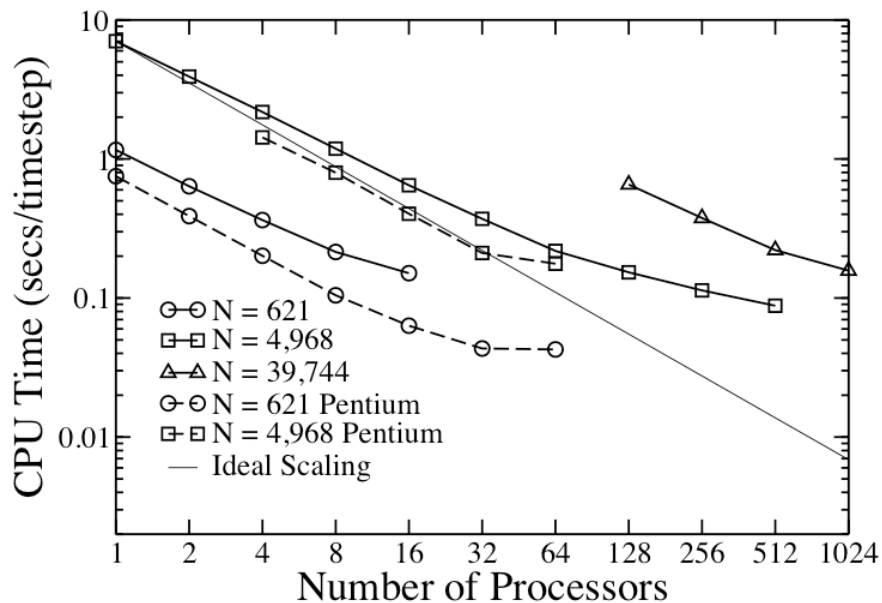
- ReaxFF is incorporated in the Grasp-framework (Aidan Thompson, Sandia) allowing parallel ReaxFF-simulations.
- LAMMPS/ReaxFF parallel program now downloadable as open-source

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/SiO₂, 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

Parallel ReaxFF: USC-Caltech-Ames collaboration

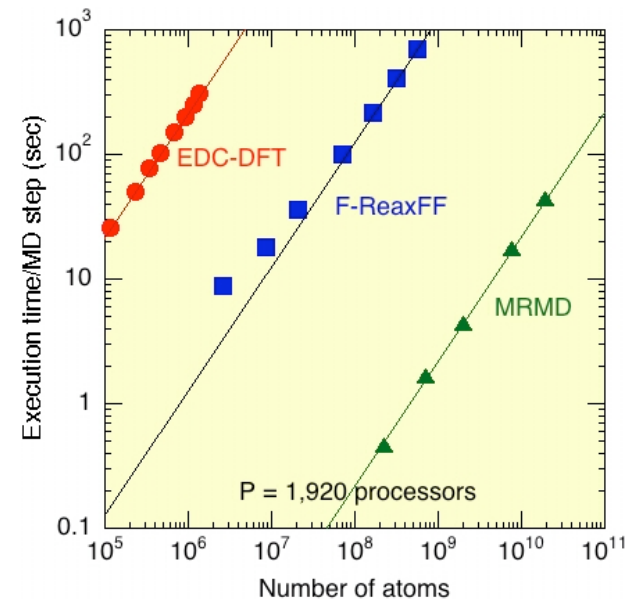
USC-Caltech-NASA Ames collaboration

Design-space diagram on
1,920 Itanium2 (1.5GHz) procs. of
NASA Columbia



Parallel efficiency as high as 0.953

- 19 billion-atom classical multiresolution MD (MRMD) of SiO_2
- 0.56 billion-atom fast reactive force-field (F-ReaxFF) MD of RDX
- 1.4 million-atom (0.12 trillion grid points) embedded divide-&-conquer (EDC)-density functional theory (DFT) MD of Al_2O_3



A divide-and-conquer/cellular-decomposition framework for
million-to-billion atom simulations of chemical reactions

Aiichiro Nakano ^{a,*}, Rajiv K. Kalia ^a, Ken-ichi Nomura ^a, Ashish Sharma ^a,
Priya Vashishta ^a, Fuyuki Shimojo ^{a,b}, Adri C.T. van Duin ^c,
William A. Goddard ^c, Rupak Biswas ^d, Deepak Srivastava ^d

^a Collaboratory for Advanced Computing and Simulations, Department of Computer Science, Department of Physics & Astronomy,
Department of Chemical Engineering & Materials Science, University of Southern California, Los Angeles, CA 90089-0242, USA

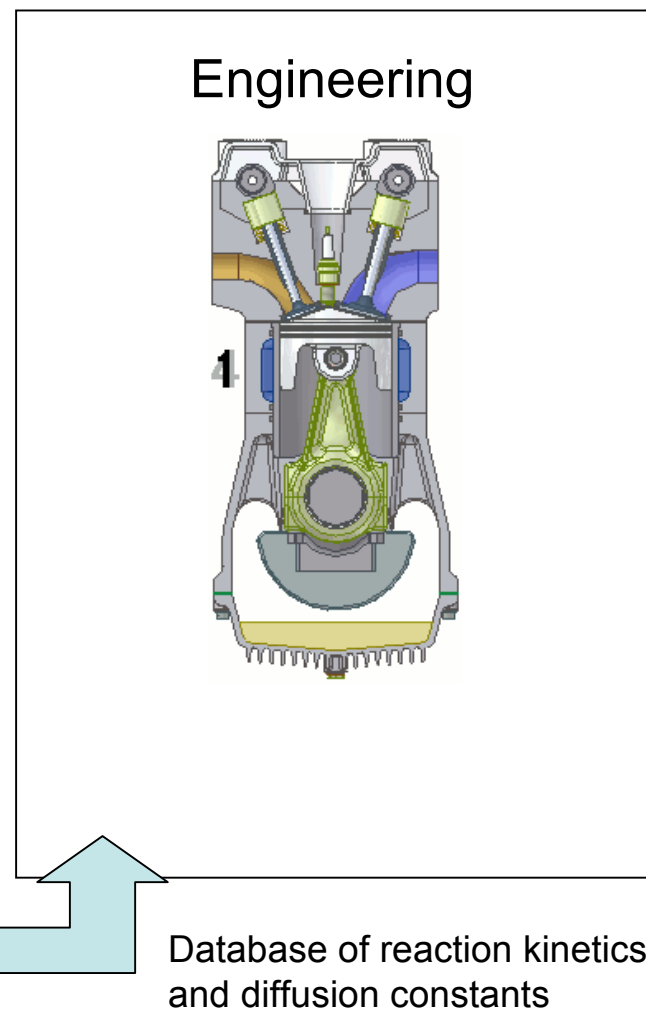
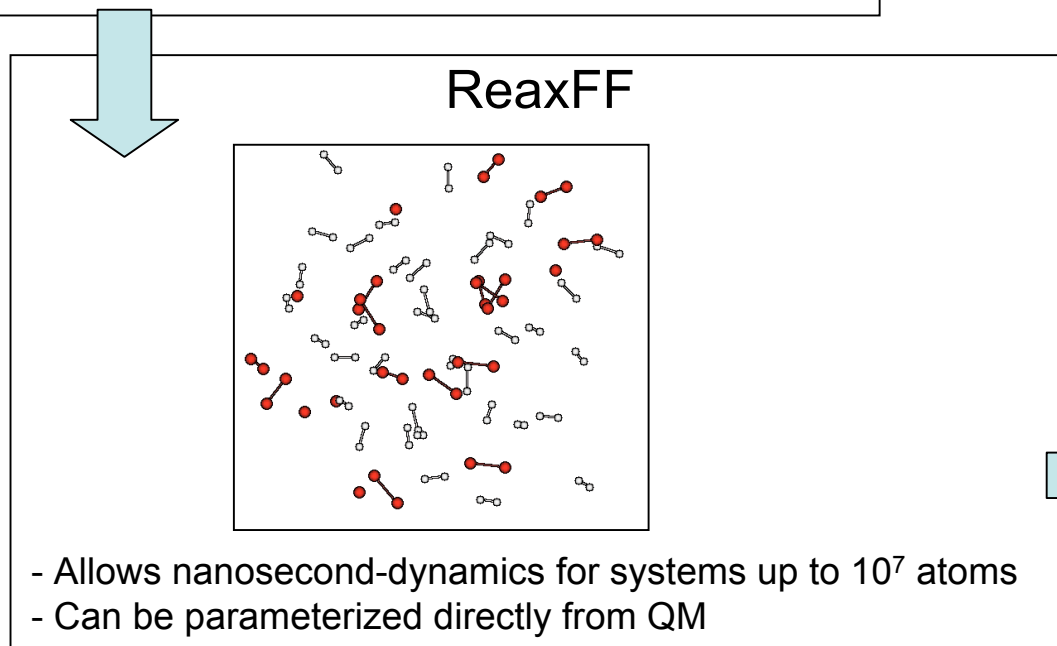
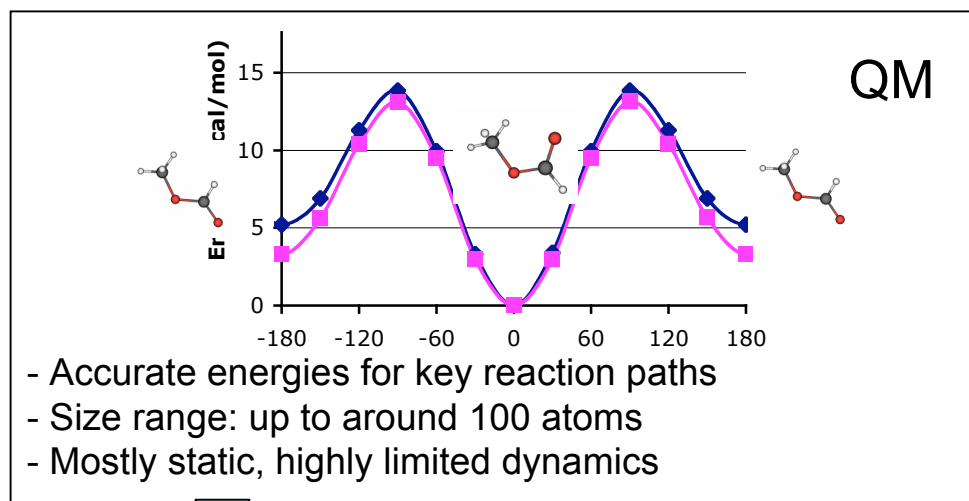
^b Department of Physics, Kumamoto University, Kumamoto 860-8555, Japan

^c Materials and Process Simulation Center, Division of Chemistry and Chemical Engineering, California Institute of Technology, Pasadena, CA 91125, USA

^d NASA Advanced Supercomputing (NAS) Division, NASA Ames Research Center, Moffett Field, CA 94035, USA

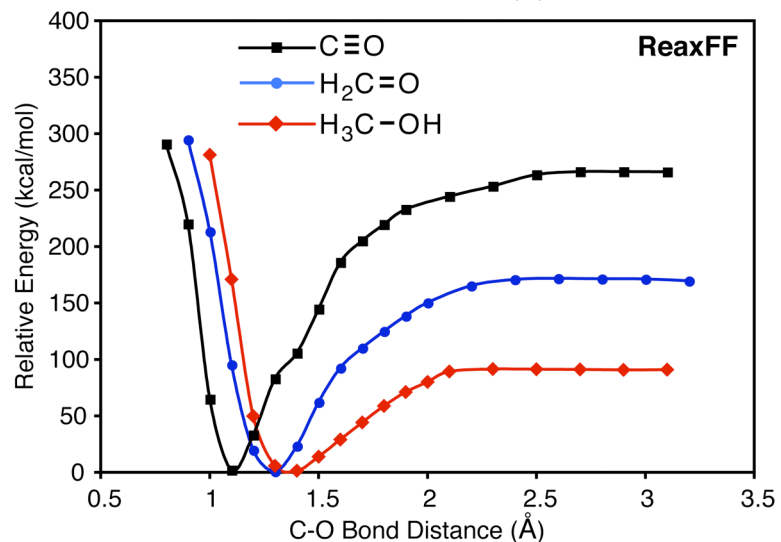
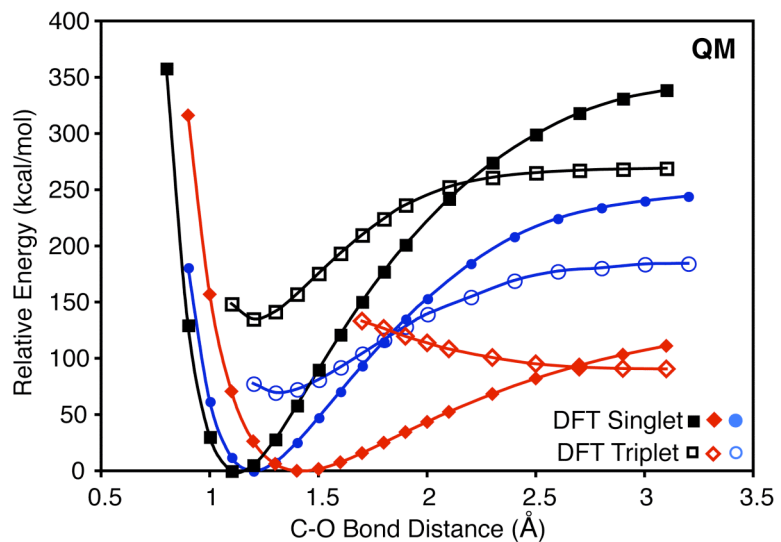
Received 22 February 2006; accepted 21 April 2006

Applications to combustion reactions

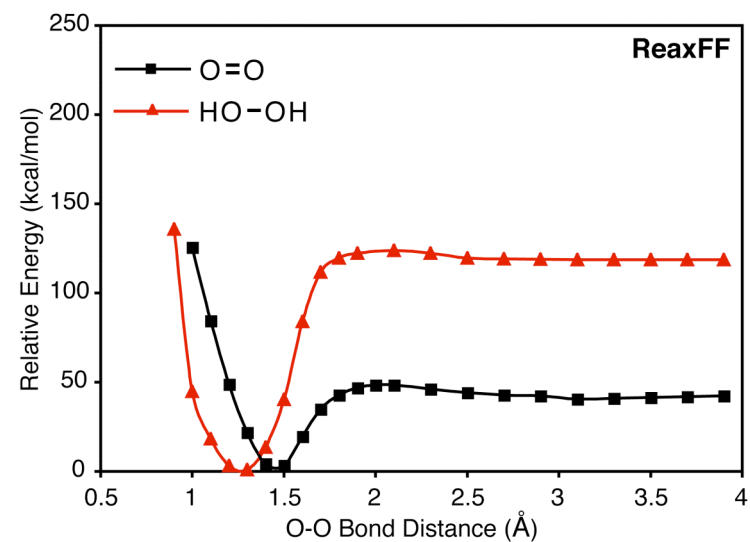
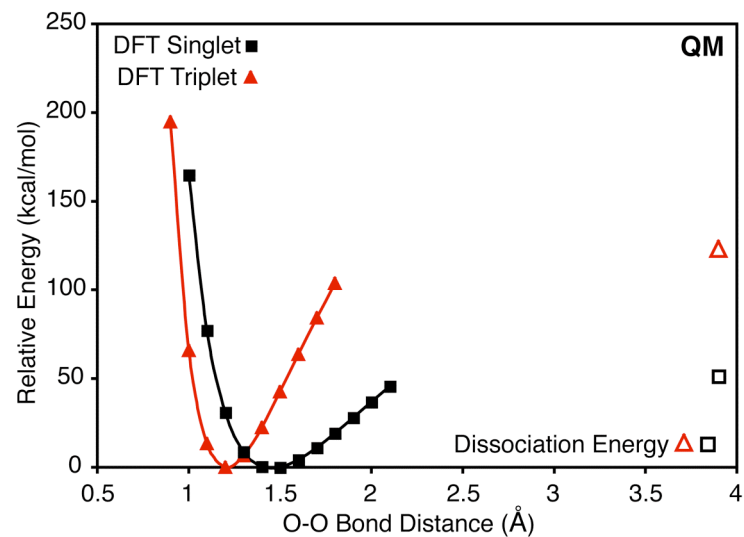


Force field development: bond dissociation curves

C-O bonds

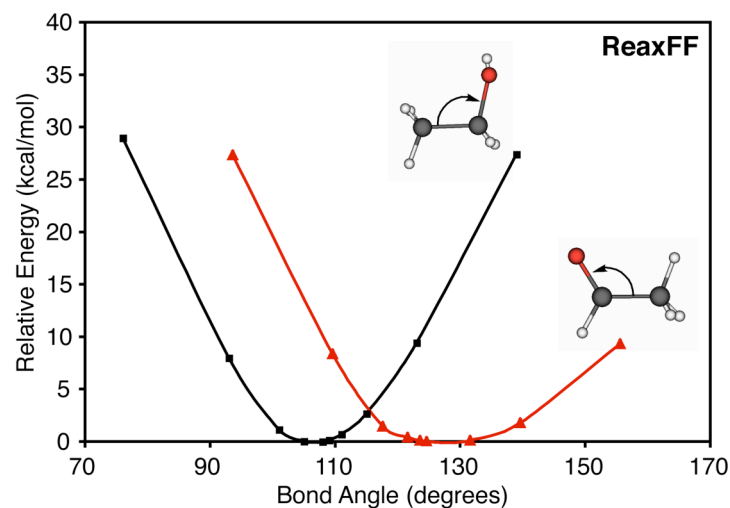
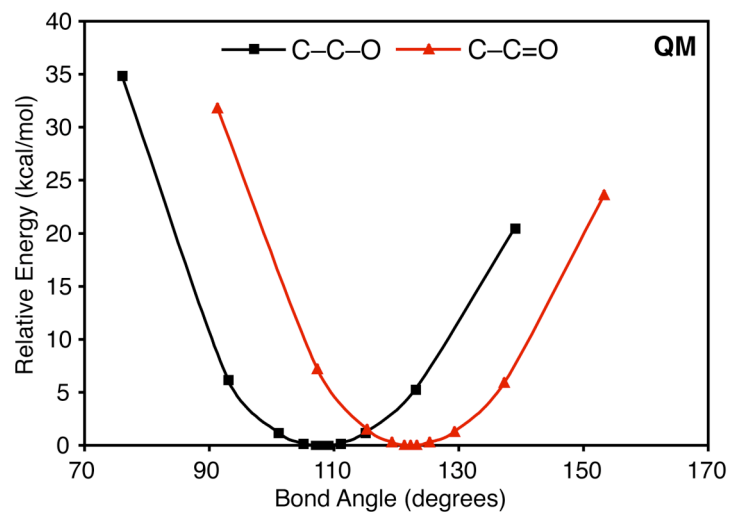


O-O bonds

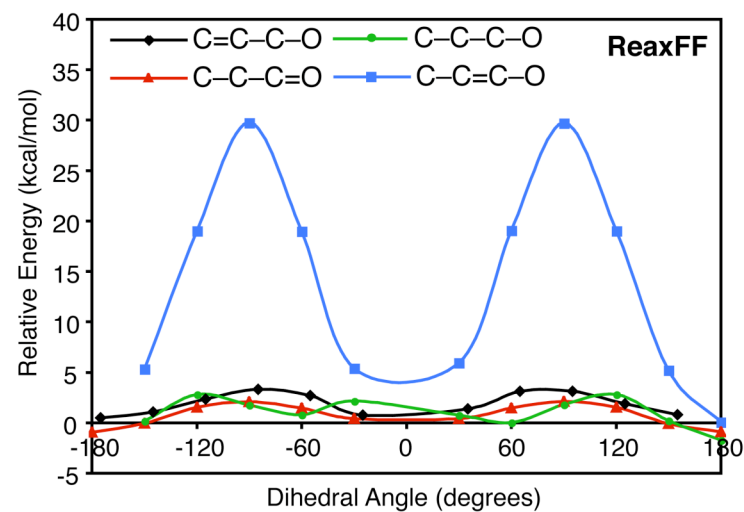
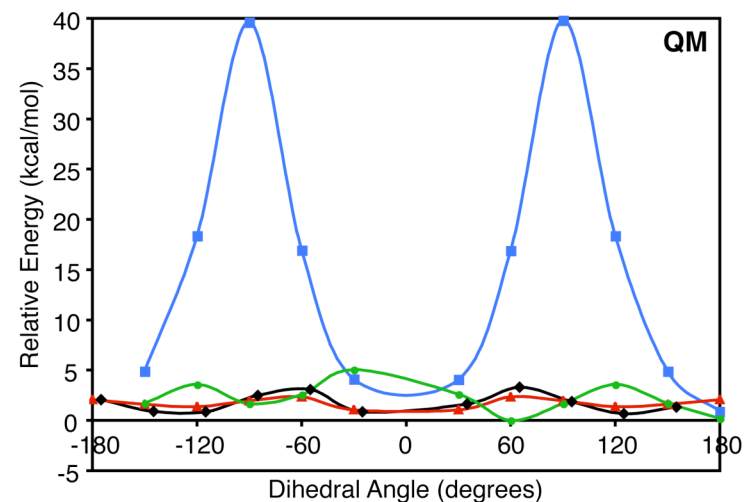


Force field development: valence and torsion angles

Valence angles

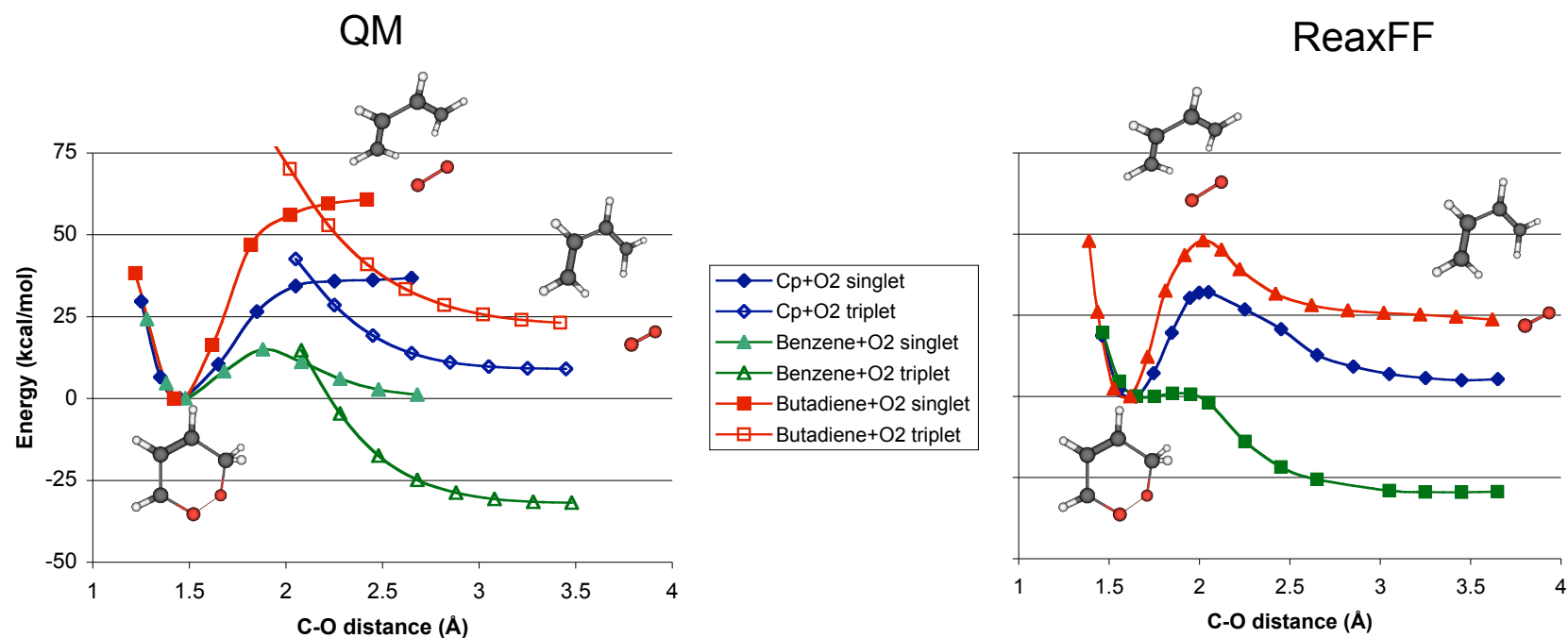


Torsion angles



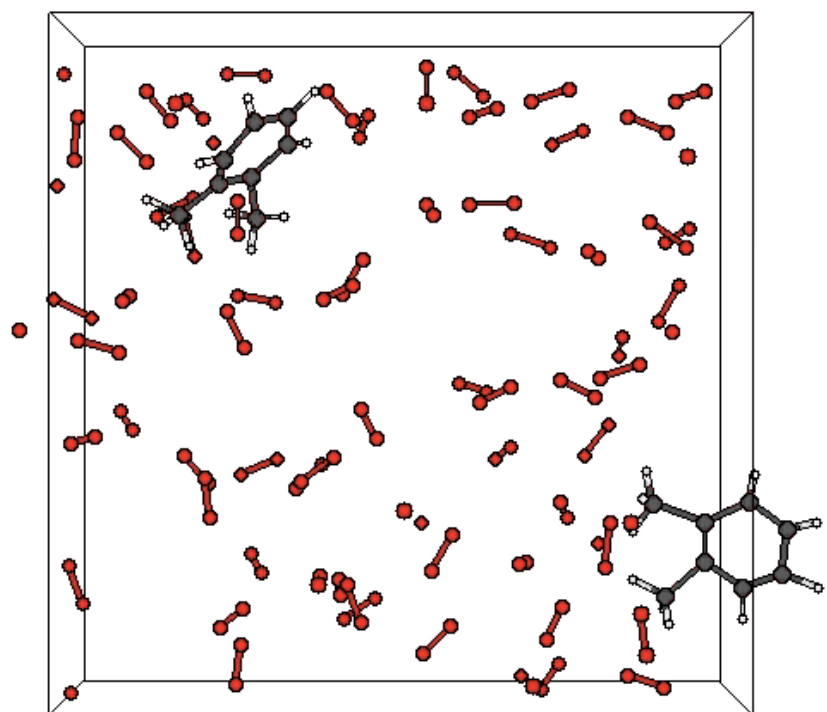
- For all C/H/O combinations
- Separate cases for single and double bonds

Force field development: reaction barriers

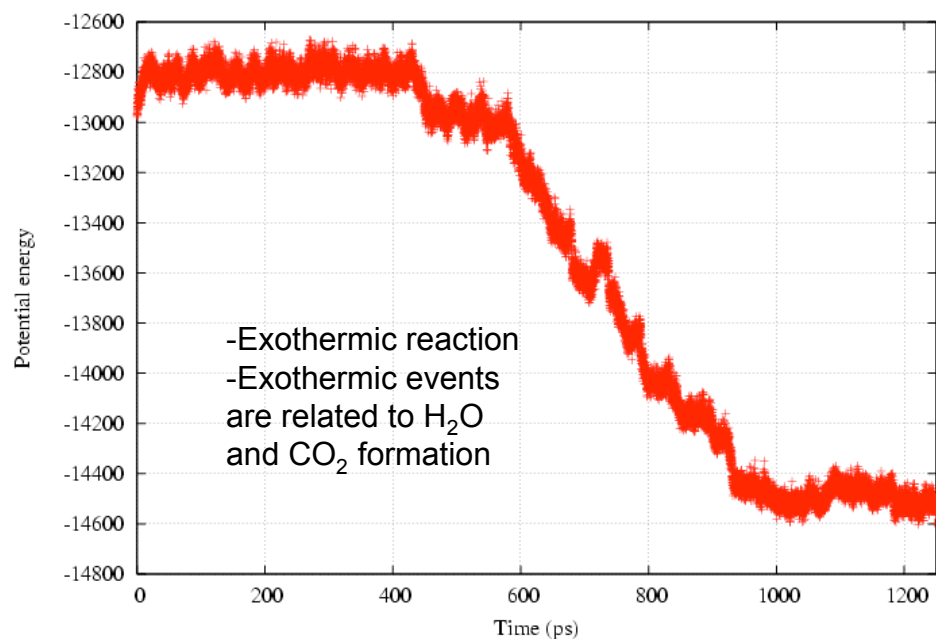
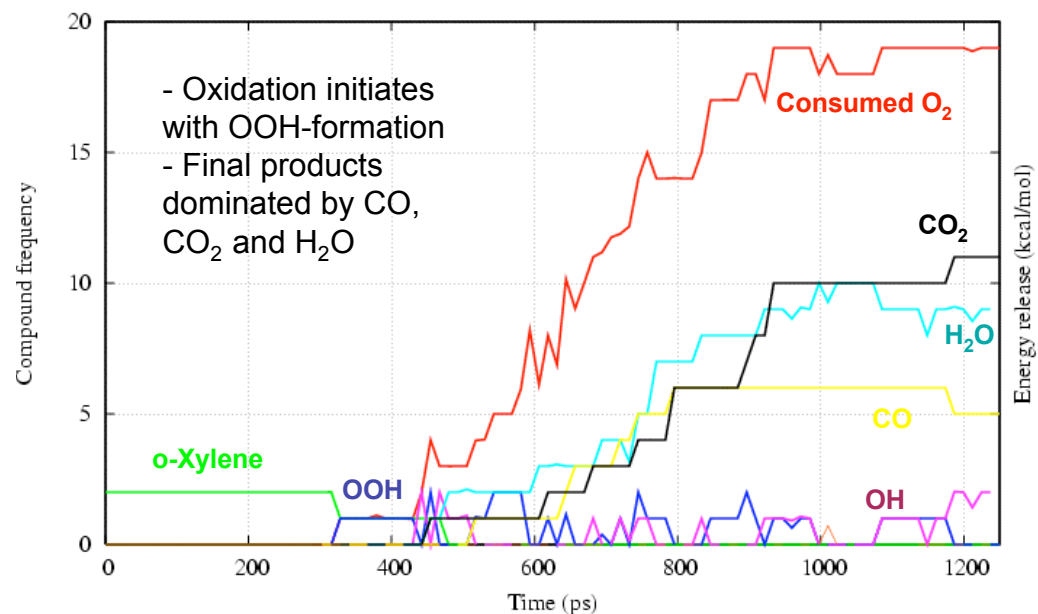


- total training set contains about 1700 compounds

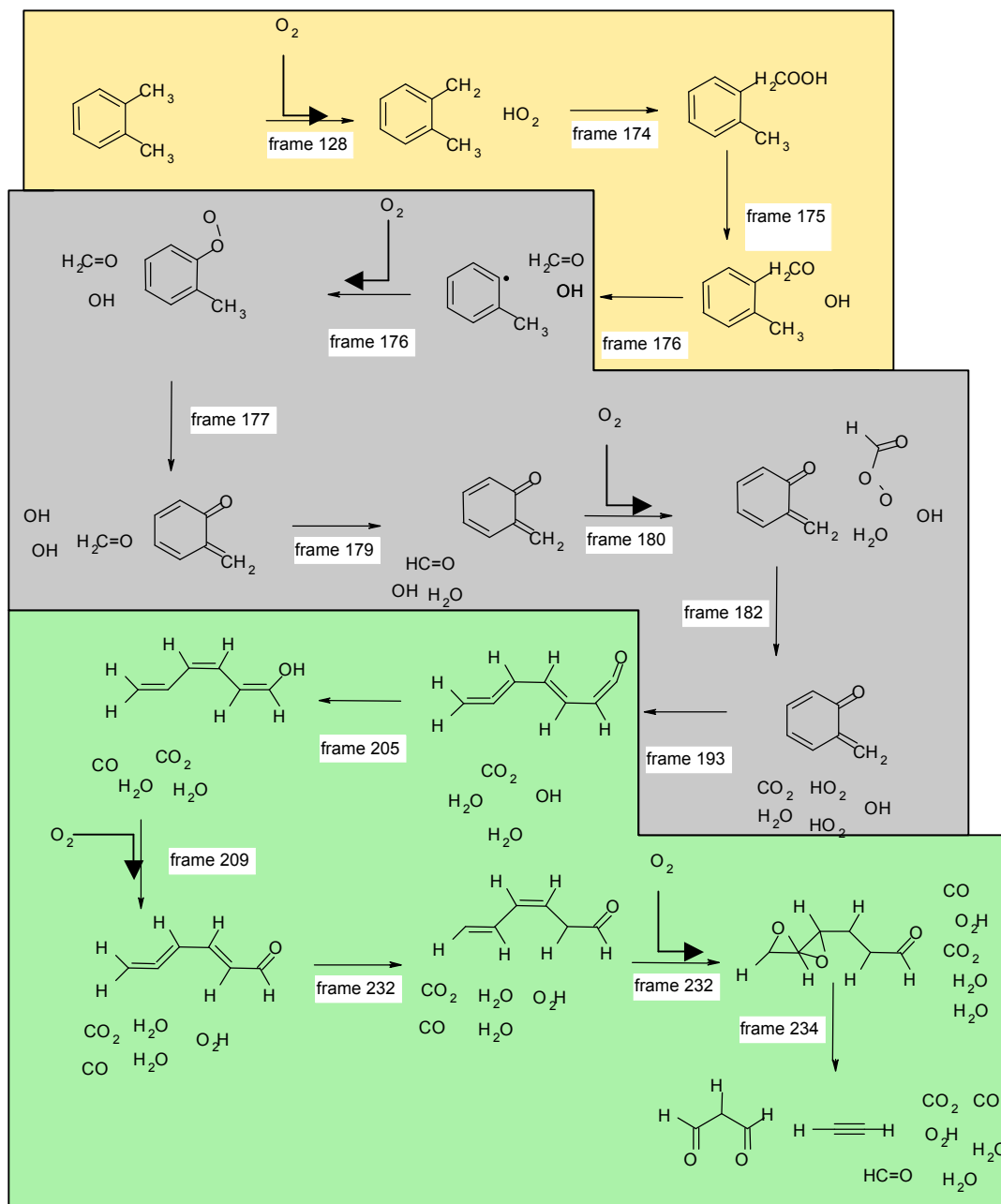
Test ReaxFF CHO-description: oxidation of o-xylene



2 o-Xylene; 70 O₂ in 20x20x20 Angstrom box
ReaxFF NVT/MD at T=2500K



o-Xylene oxidation: Detailed reaction mechanism



- Reaction initiation with HO_2^- formation

- Dehydrogenation occurs at methyl-groups, not at benzyl-hydrogens

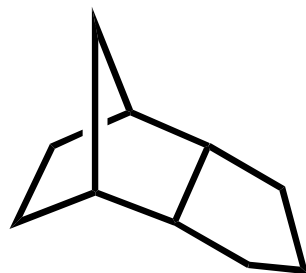
- Only after $H_2C=O$ is formed and dissociated the benzene ring gets oxidized

- Ring opens shortly after destruction of aromatic system

- Ring-opened structure reacts quickly with oxygen, forming CO_2 , H_2O and CO

- ReaxFF gives sensible predictions that can be directly tested against QM

Initiation Mechanism and Kinetics for Pyrolysis and Combustion of JP-10

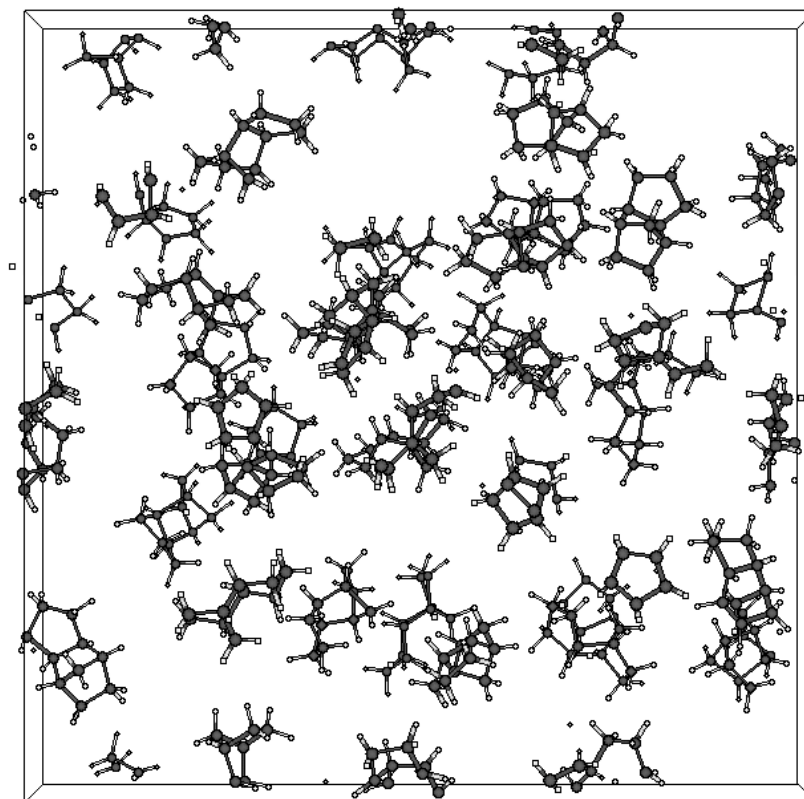


Exo-tetrahydrodicyclopentadiene: JP-10

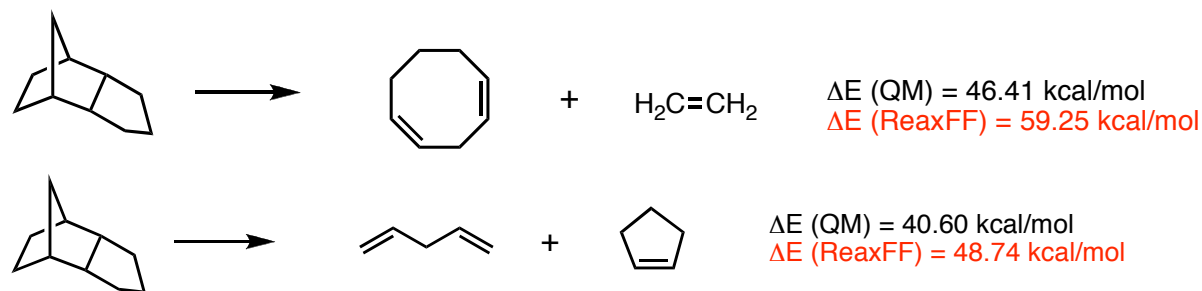
- **Synthetic high-energy density fuel**
 - Volumetric heat content: 39434 MJ/m³ (141500 BTU/gal); high strain leads to high energy output
 - Potential use in pulse detonation engines and missile applications
 - Single component fuel
- **Mechanism is incomplete**
 - No clean mechanism for either pyrolysis and combustion
 - Early stages of fragmentation and oxidation are important for combustion models
- **Goal**
 - Use ReaxFF to predict initiation mechanisms and kinetics
 - Validate predictions with QM and experiment

Simulation strategy for JP-10 pyrolysis

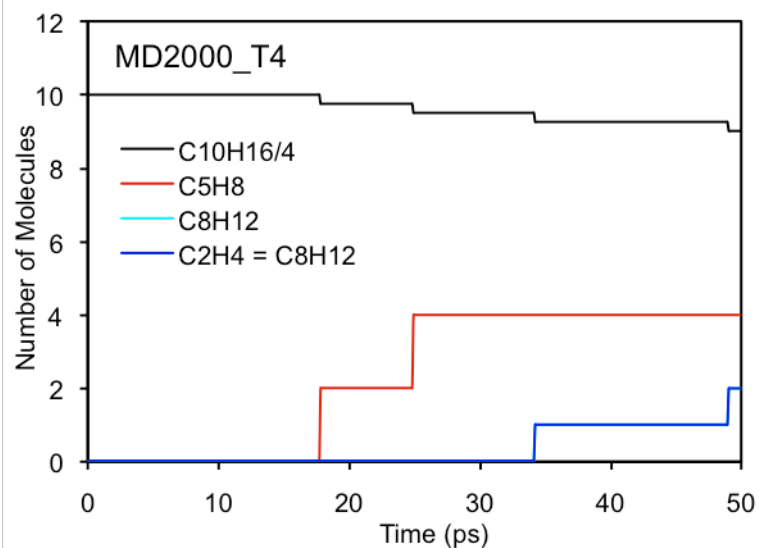
- **40 JP-10 Molecules (1040 atoms)**
- **Density = 0.388 g/cm³**
- Equilibrated at 1500K for 10 ps
- Temperature control using Berendsen thermostat with 0.1 ps damping constant
- MD time step of 0.1 fs
- **Total simulation time: 50 ps**
- Perform a series of NVT-MD simulations to calculate activation energy and product distribution
 - **Temperature (K): 2000, 2100, 2200, 2300, 2400, 2500, 2600**
 - 10 simulations at each temperature with unique starting configuration
 - Results obtained by averaging over the 10 simulations at each temperature



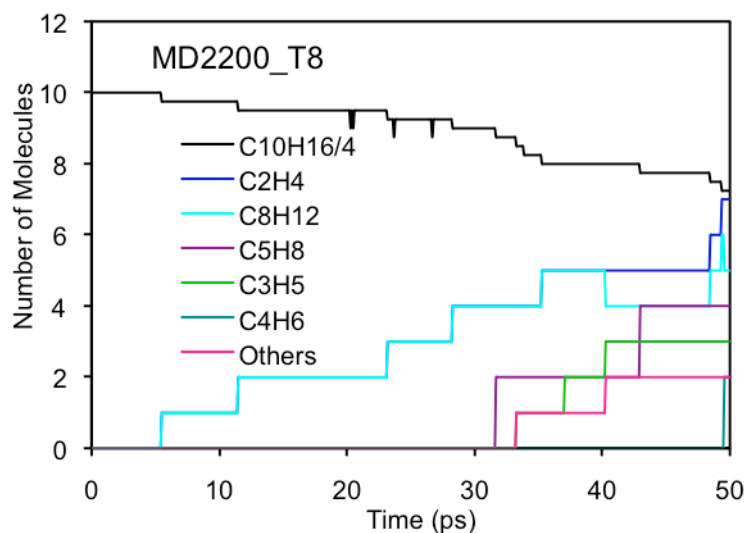
JP-10 pyrolysis: product distributions



T=2000K; run 4

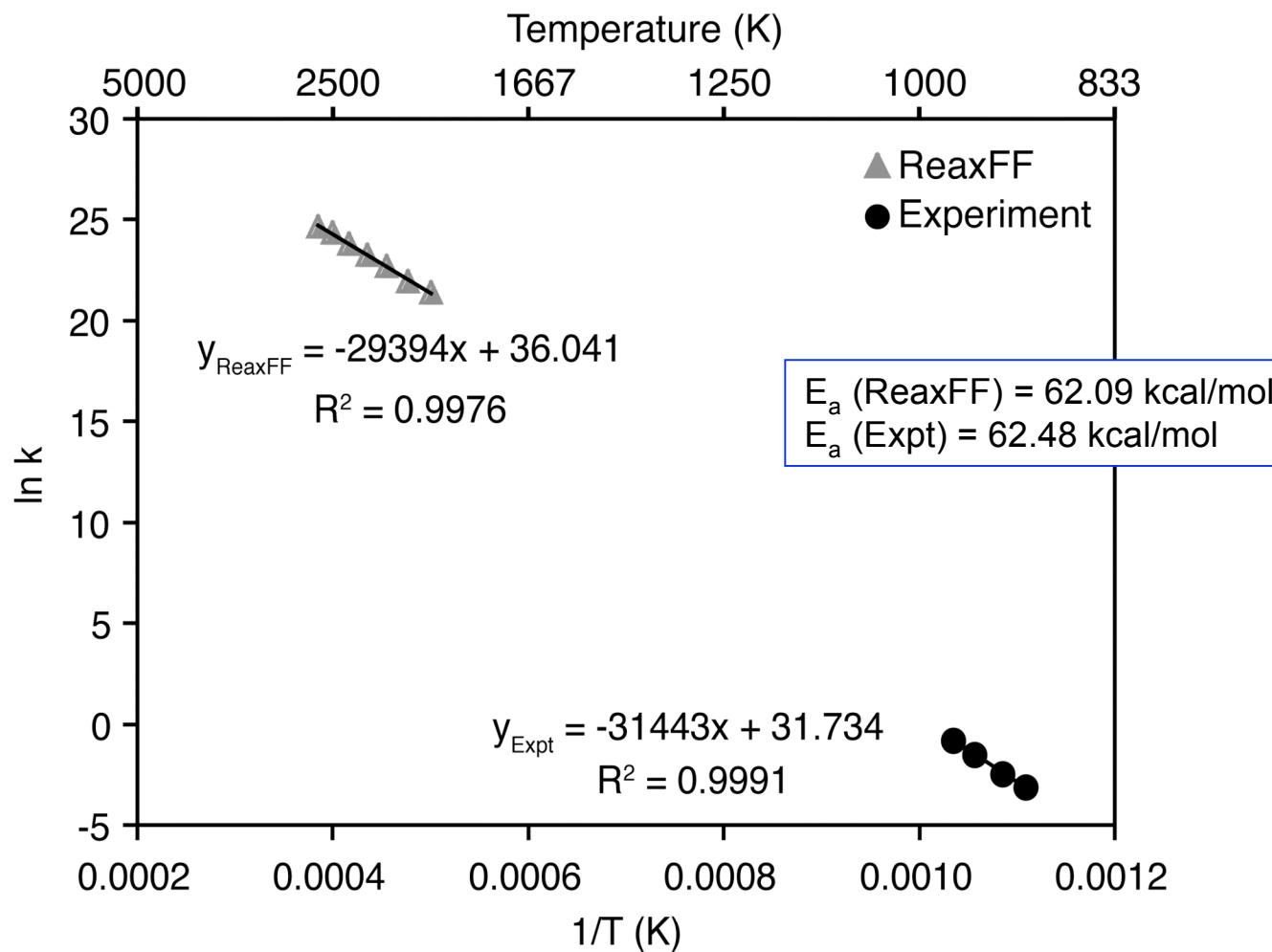


T=2200K; run 8



- Initiation reactions: good agreement between QM and ReaxFF
- Elevated temperatures leads to enhanced $\text{C}_2\text{H}_4/\text{C}_8\text{H}_{12}$ production

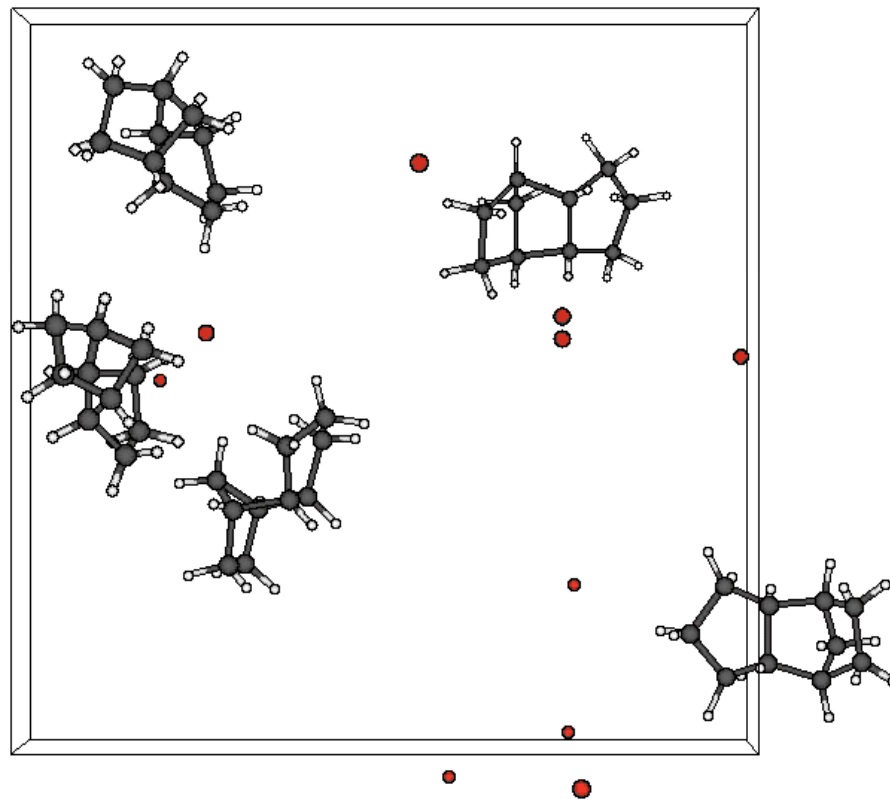
Kinetics for JP-10 Pyrolysis



- Excellent agreement with experiment (Rao and Kunzru, J. Anal. Appl. Pyrolysis 2006)

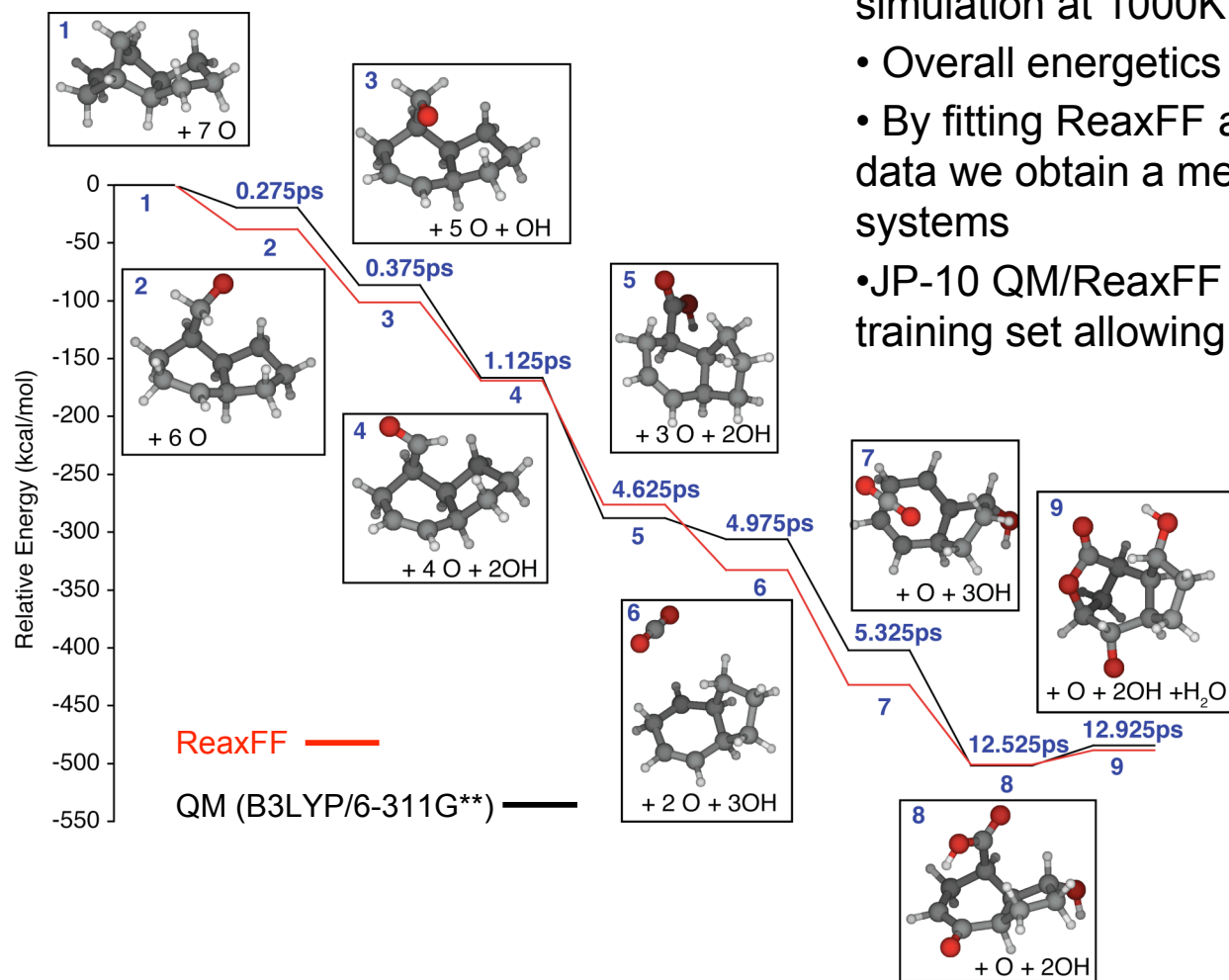
Simulation strategy for JP-10 oxidation

- **5 JP-10 molecules**
- **10 oxygen radicals**
- 140 atoms
- Density = 0.174 g/cm³
- Equilibrated at 1000K for 5 ps
- Temperature control using Berendsen thermostat with 0.1 ps damping constant
- MD time step of 0.1 fs
- **Total simulation time: 10 ps**
- **Performed a NVT-MD simulation at 1000K**
- **Perform QM calculations on intermediates to validate ReaxFF results**



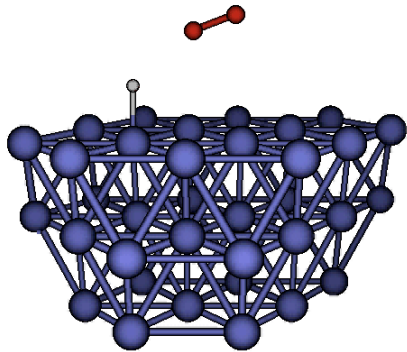
JP-10 oxidation

- Reaction mechanism observed during NVT-MD simulation at 1000K
- Overall energetics in good agreement with QM
- By fitting ReaxFF against a large database of QM-data we obtain a method that is transferable to new systems
- JP-10 QM/ReaxFF comparison can be fed back into training set allowing the force field to further improve



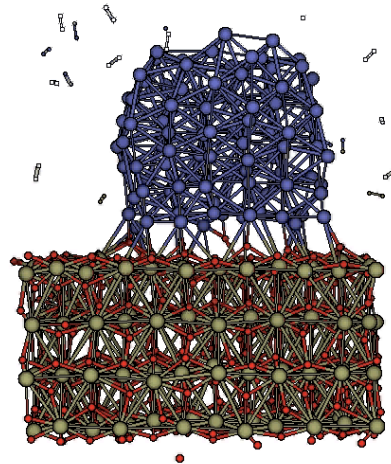
Applications to surface catalysis

QM



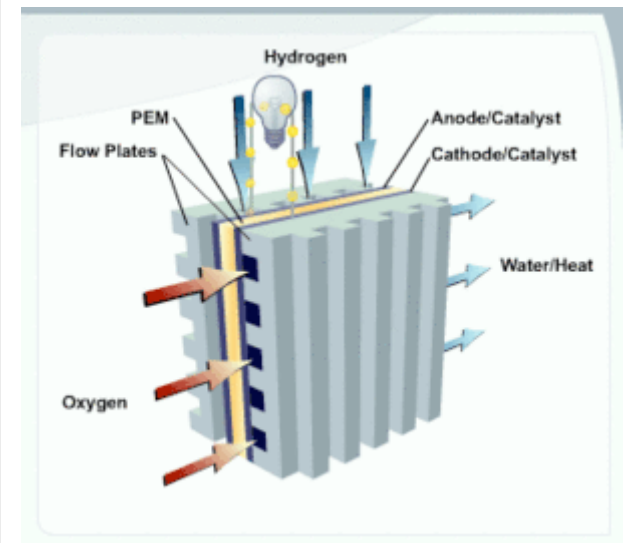
- Accurate energies for key reaction paths
- Size range: up to around 100 atoms

ReaxFF



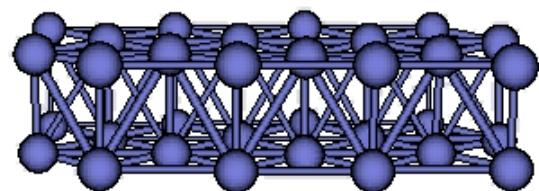
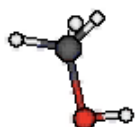
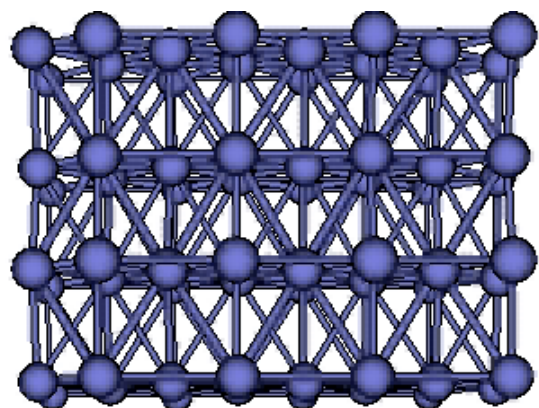
- Allows nanosecond-dynamics on multi-component systems
- Can be parameterized directly from QM

Engineering

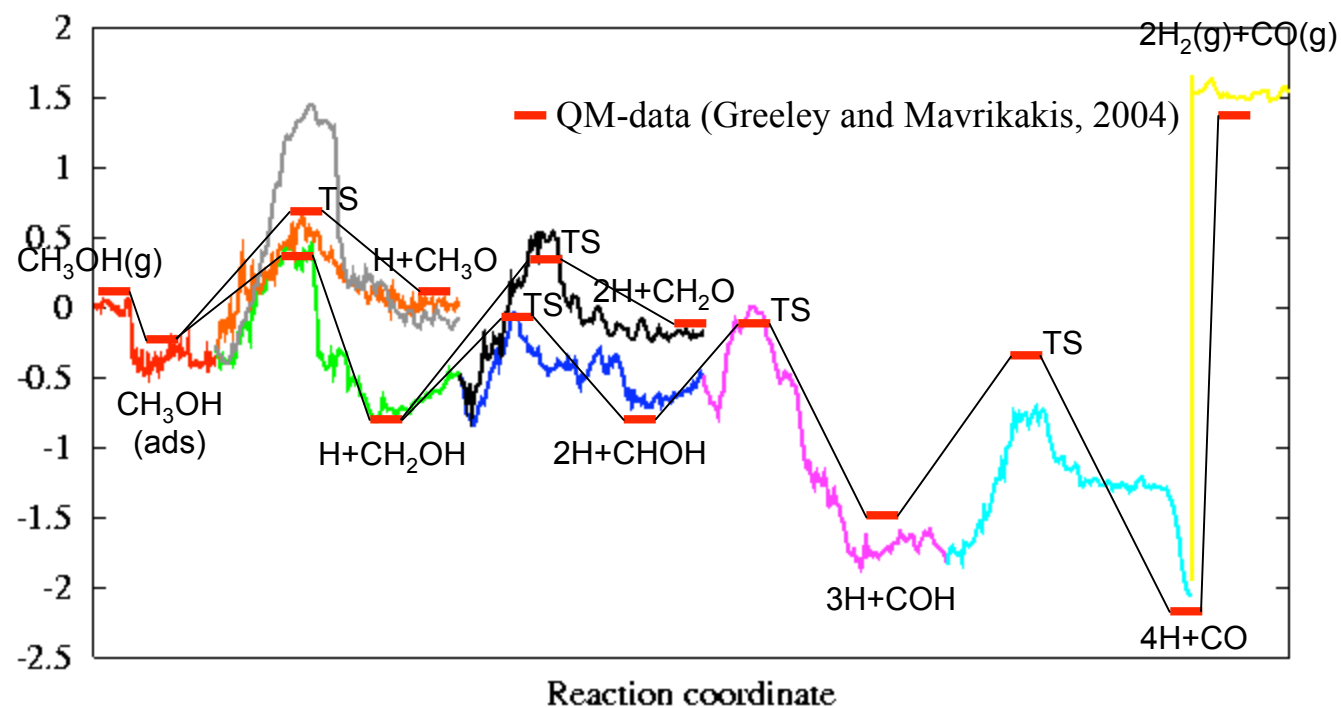


- Interface properties
- Reaction kinetics
- Diffusion constants

QM/ReaxFF methanol reaction pathways



Methanol reaction on Pt[111] surface

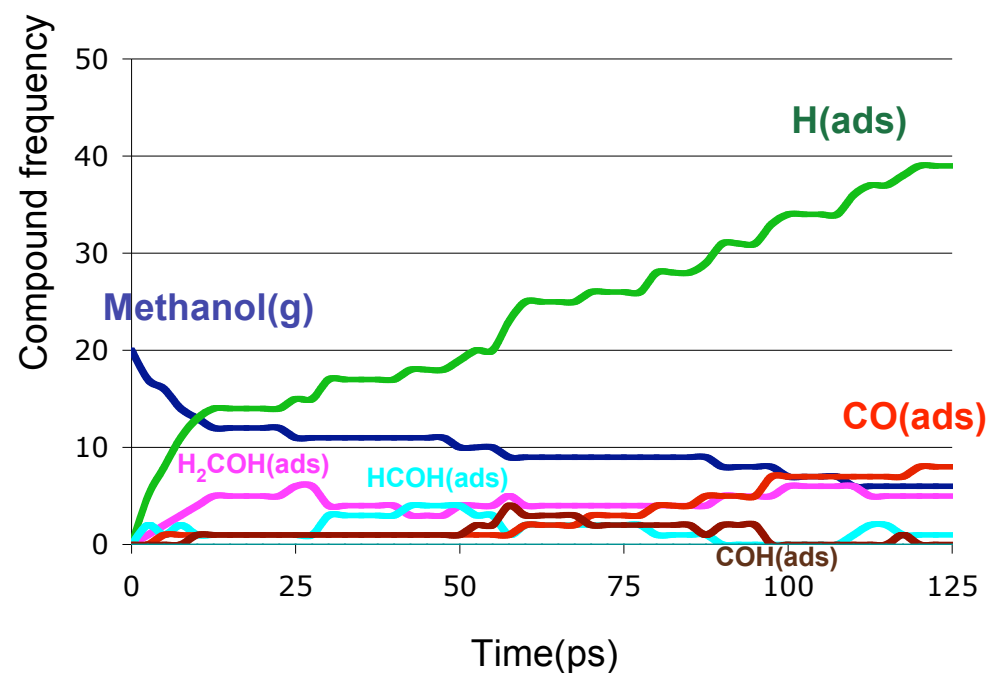
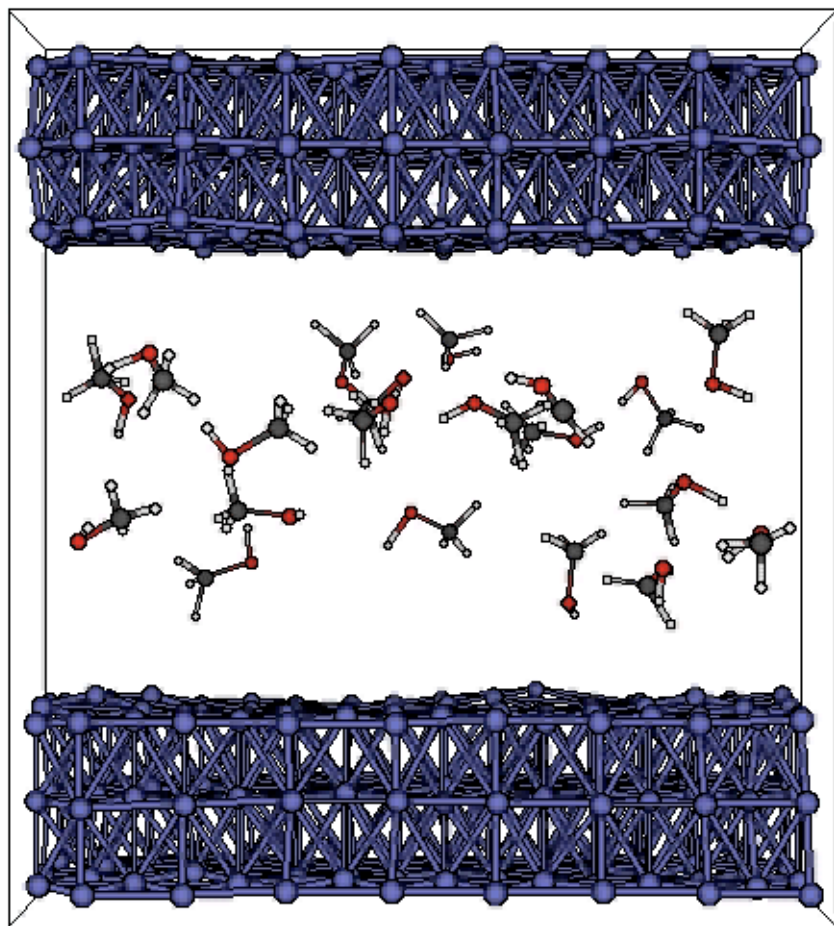


H ₃ COH(g) → H ₃ COH(ads)	—	CO(g)+2H ₂ (g)	—
H ₃ COH(ads) → H ₂ COH+H	—	H ₂ COH+H → H ₂ CO+2H	—
H ₂ COH+H → HCOH+2H	—	H ₃ COH(ads) → H ₃ CO+H	—
HCOH+2H → COH+3H	—	H ₃ COH(ads) → H ₃ C+OH	—
COH+3H → CO+4H	—		

- Excellent agreement between ReaxFF and QM for entire reaction path

Methanol conversion on Pt[111]-surface

MD-simulation at T=1250K on methanol/Pt[111]




- Methanol dissociates on Pt-surface, generating adsorbed hydrogen
- CO accumulates on surface (poisoning)
- ReaxFF descriptions for Ti, Mo, V, Bi, Ru, Ni available

Summary

- 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.

group	1*	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
period	Ia	IIa	IIIa**	IVa	Va	VIa	VIIa	VIIIa	VIIIa	VIIIa	Ib	IIb	IIIb	IVb	Vb	VIb	VIIb	VIIIb
1	H	He																
2	Li	Be																
3	Na	Mg																
4	K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr
5	Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe
6	Cs	Ba	La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn
7	Fr	Ra	Ac															

 : not currently described by ReaxFF

Acknowledgements

Collaborators:

Penn State: Mike Russo, Satyam Agrawalla, Arvind Bharati, Amar Kumat, Kaushik Joshi

Caltech: William Goddard, Boris Merinov, Kimberley Chenoweth, Jonas Oxgaard, Mu-Jeng Cheng

Timo Jacob (Ulm), Aiichiro Nakano (USC), Aidan Thompson (Sandia), Ananth Grama (Purdue)

More information on ReaxFF:

<http://www.mne.psu.edu/vanduin>

E-mail: acv13@psu.edu

