Reactive Molecular Dynamics Modeling and Advanced Power Generation Applications

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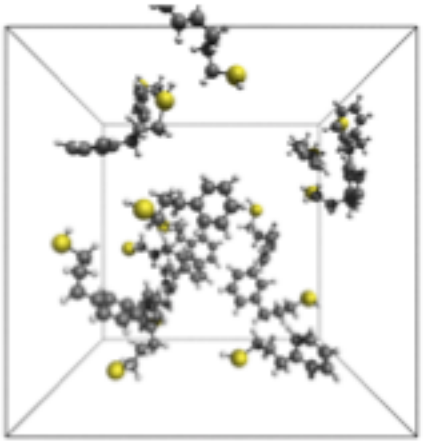
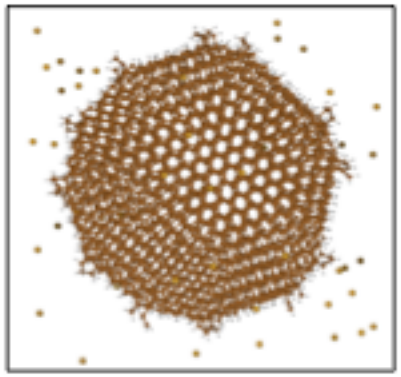
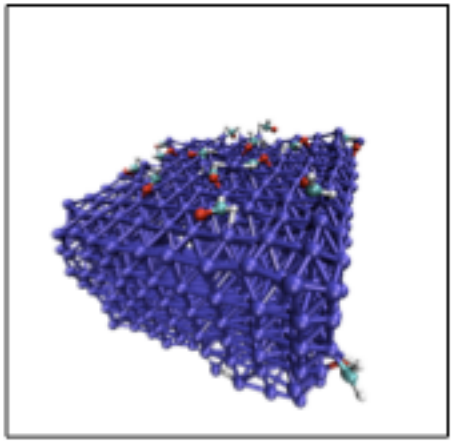


Pyrolysis of a sulphurized hydrocarbon mixture



Noble gas accomodation coefficients on a graphene wafer



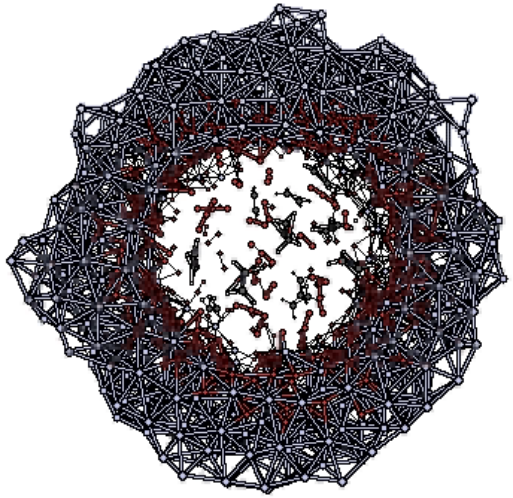
Conversion of formaldehyde on a iron particle

2010 UTSR meeting, October 21 2010

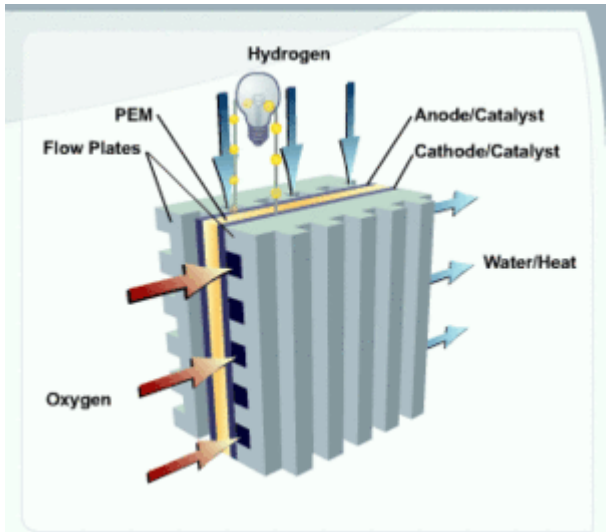
Engineering challenges….

Coal power plant

- Higher efficiency
- Lower exhaust
- Higher combustion temperature
- Need new materials that can sustain higher temperatures and oxidation chemistry

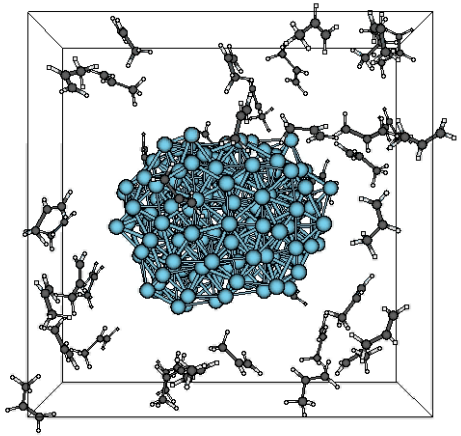


Pre-oxidized Al-tube with ethylene/O_2/ozone mixture



Fuel cell

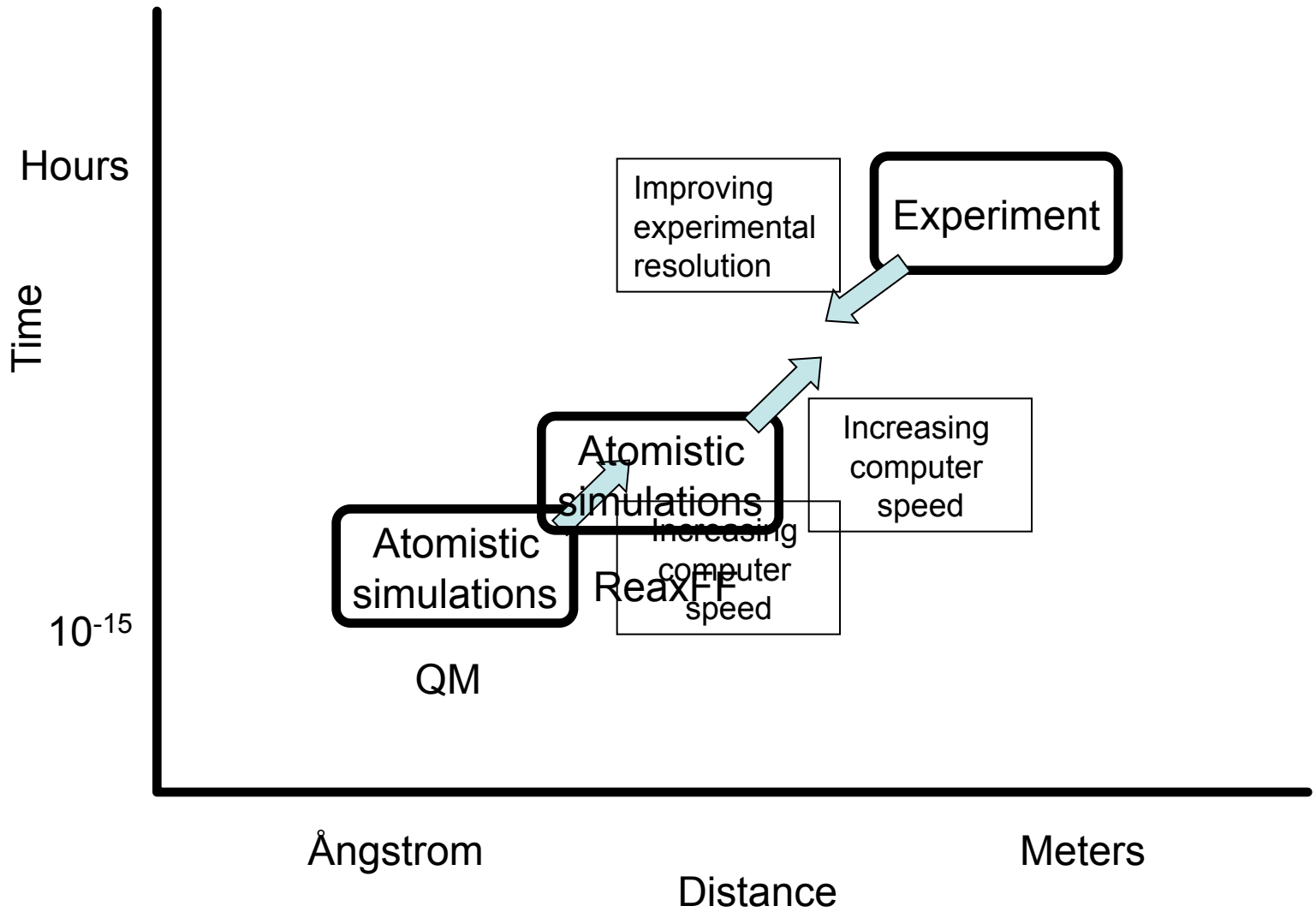
- Higher efficiency
- Longer lifetime
- Cheaper
- Need new, cheap catalyst materials that are resistant to poisoning



Ni-particle reacting with propene at T=1500K

…require atomistic-scale solutions

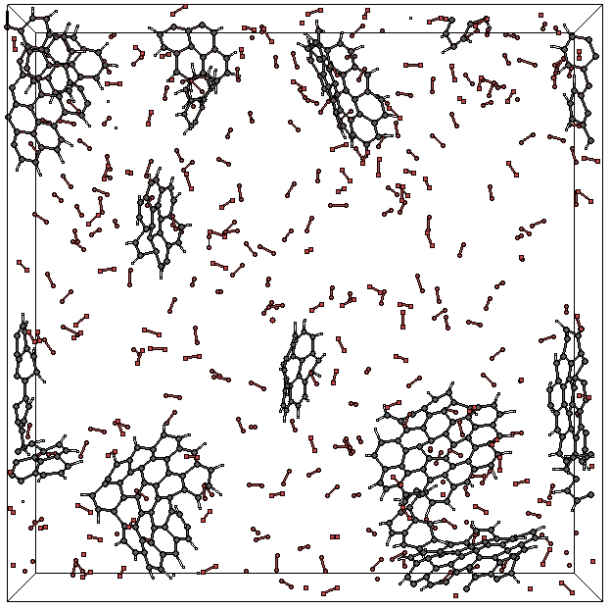
Solving the size/time gap between simulation and experiment



Outline

- The ReaxFF reactive force field
- Overview of ReaxFF applications
    - Combustion reactions
    - Aqueous phase and surface chemistry

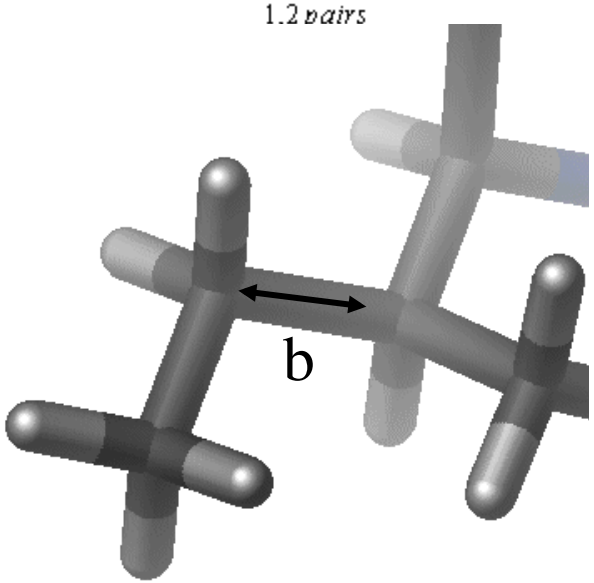
- Summary



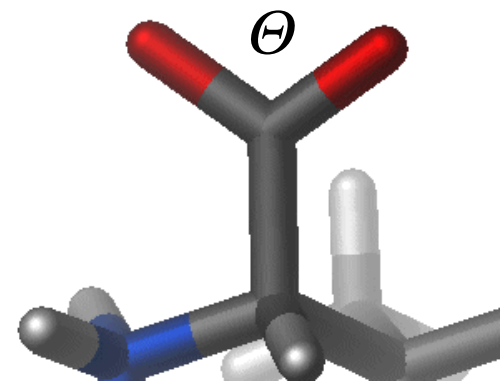
ReaxFF MD-simulation on soot combustion at elevated oxygen pressure. Soot structure provided by Jonathan Mathews (Penn State)

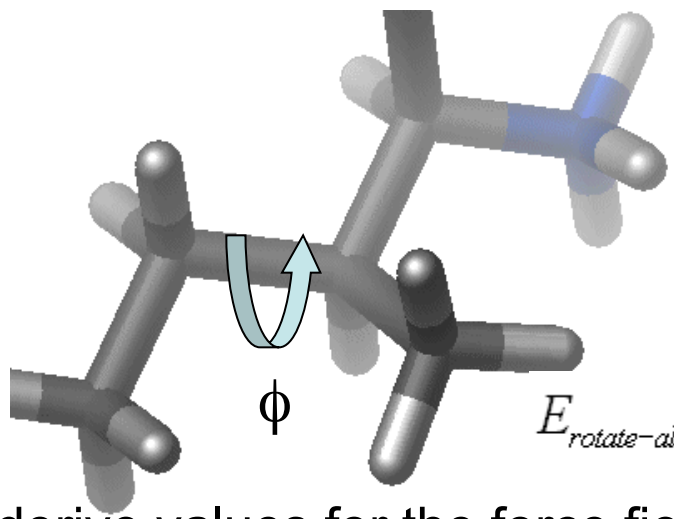
Force field methods

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



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





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

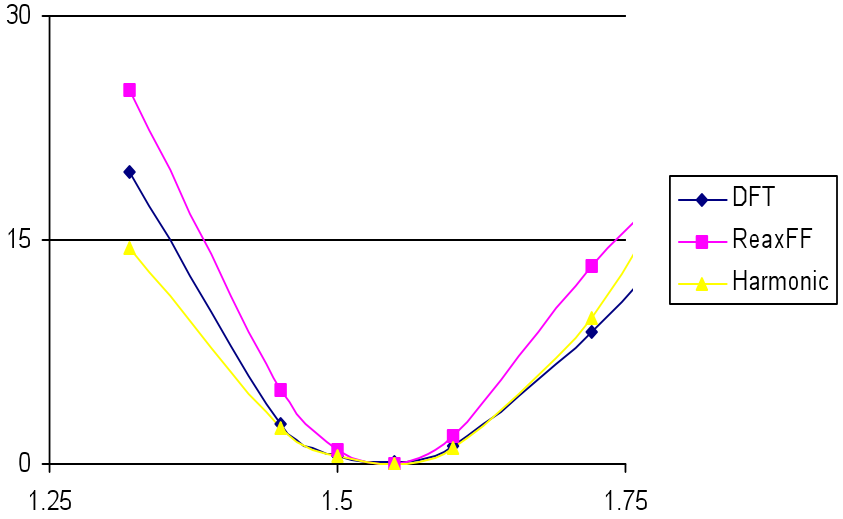
- Empirical, we need to derive values for the force field parameters (intuition, compare to experiment, compare to QM)

©2005 Markus Buehler, MIT

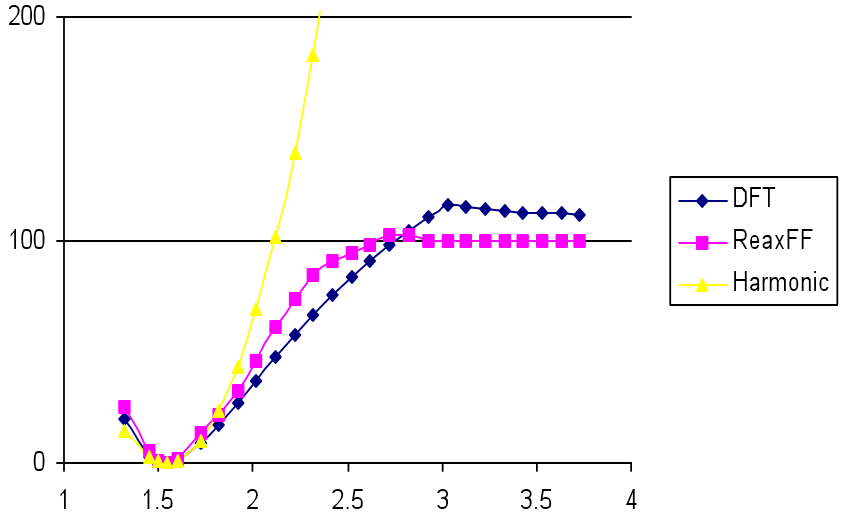
Failure of the harmonic model

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.

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 [1-3]. Bond orders are updated every iteration.

-All connectivity-dependent interactions (i.e. valence and torsion angles, H-bond) 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.

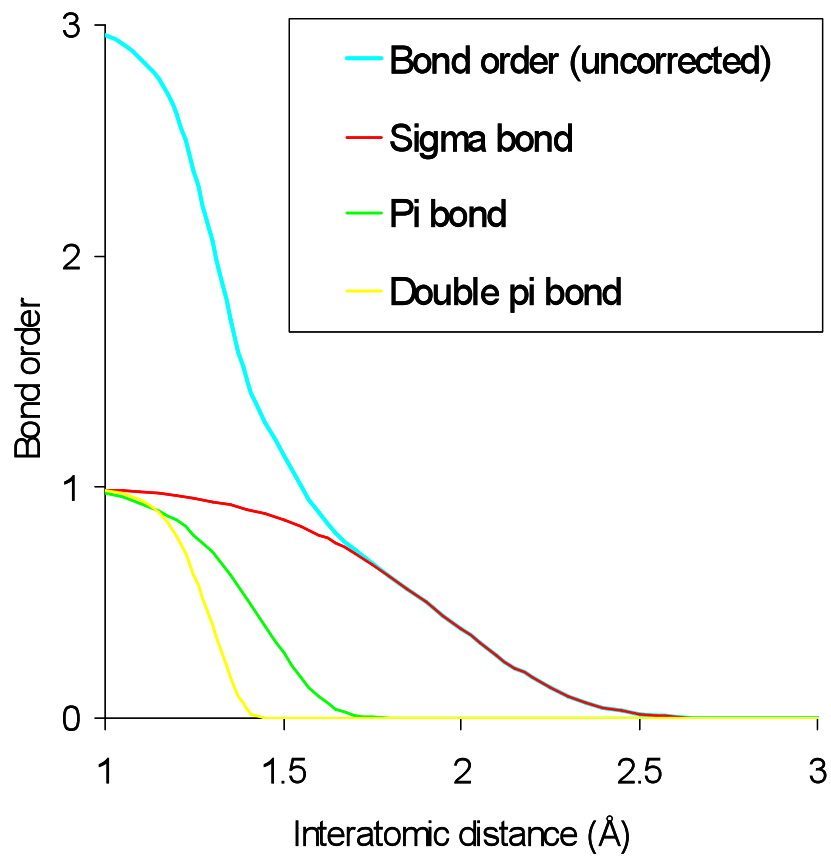
- ReaxFF uses EEM, a geometry-dependent charge calculation scheme that accounts for polarization effects [4].

1. Brenner, D. W., (1990) Physical Review B **42**, 9458-9471
2. Tersoff, J., (1988) Physical Review Letters **61**, 2879-2882.
3. Abell, G. C., (1985) Physical Review B 31.
4. Mortier, W. J., Ghosh, S. K., and Shankar, S. (1986) JACS **108**, 4315-4320.

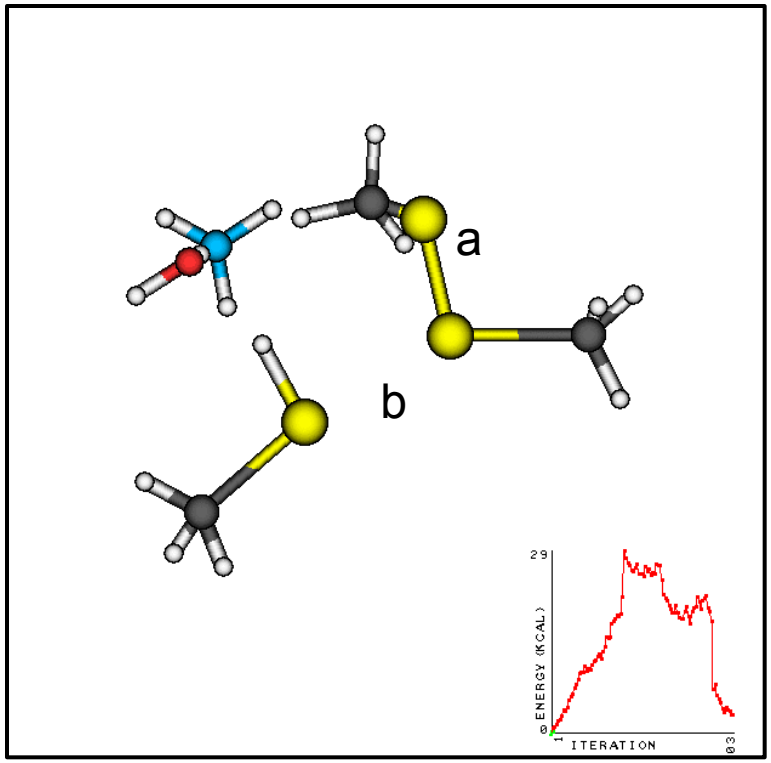
Bond orders

Calculation of bond orders from interatomic distances

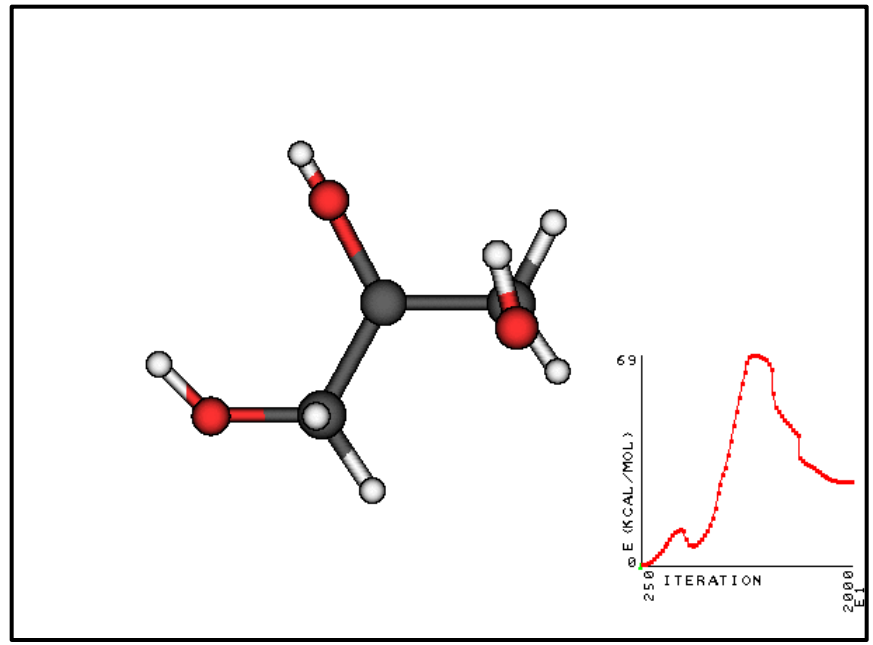
$$BO'_{ij} = \exp\left[p_{bo,1} \cdot \left(\frac{r_{ij}}{r_o^{\sigma}}\right)^{p_{bo,2}}\right] + \exp\left[p_{bo,3} \cdot \left(\frac{r_{ij}}{r_o^{\pi}}\right)^{p_{bo,4}}\right] + \exp\left[p_{bo,5} \cdot \left(\frac{r_{ij}}{r_o^{\pi\pi}}\right)^{p_{bo,6}}\right]$$



ReaxFF energy barriers



ReaxFF barrier for $NH_3/H_2O/H_3CSH$ assisted disulfide cleavage (collaboration with Markus Buehler, MIT)



ReaxFF barrier for Grob fragmentation (collaboration with John Daily, Boulder). QM barrier: 65 kcal/mol (Nimlos et al., JPC-A 2006)

- Longer-range bond orders enable more accurate and transferable description of reaction energy barriers, compared to earlier reactive force field concepts.

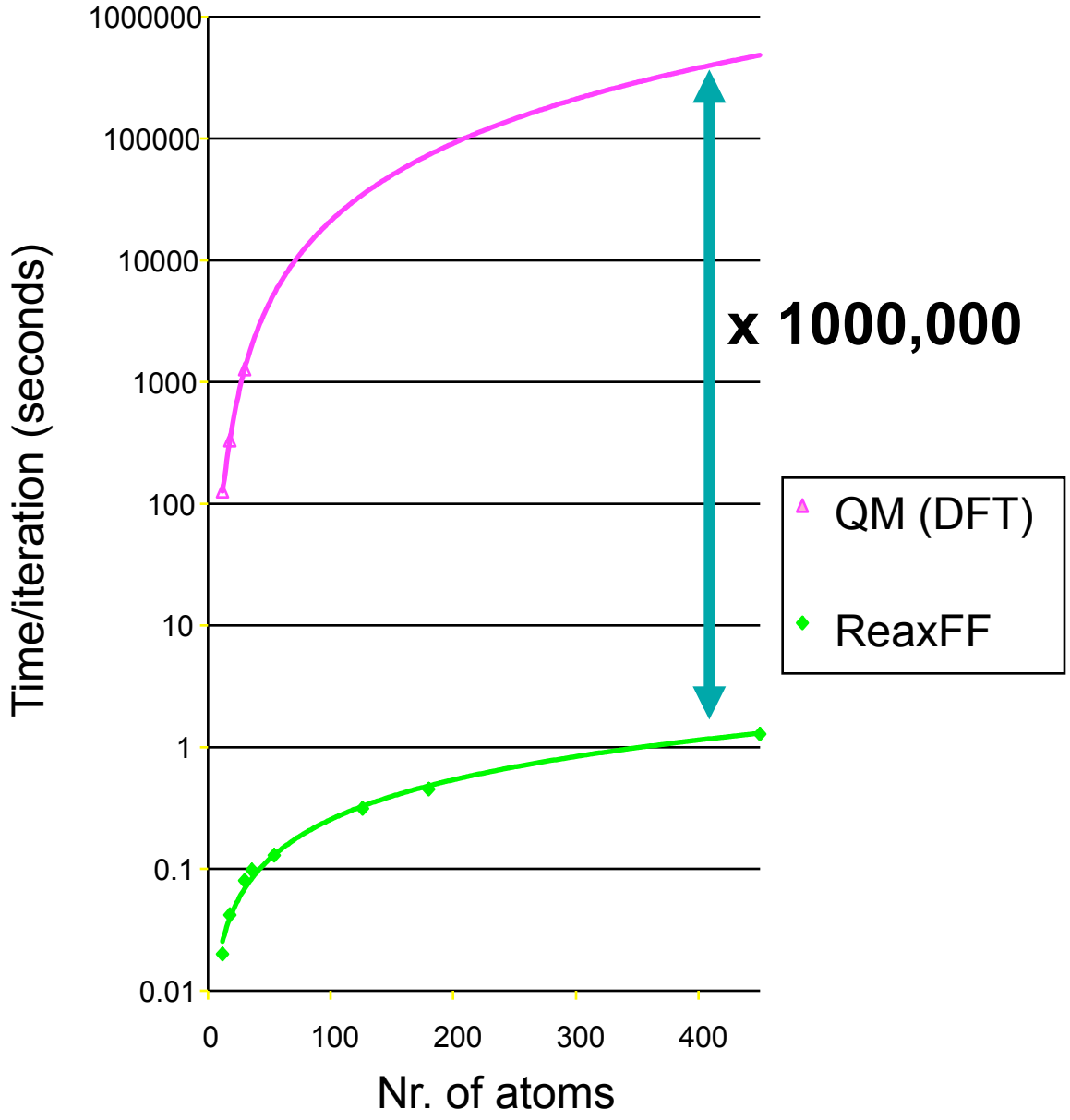
General rules for ReaxFF

- 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

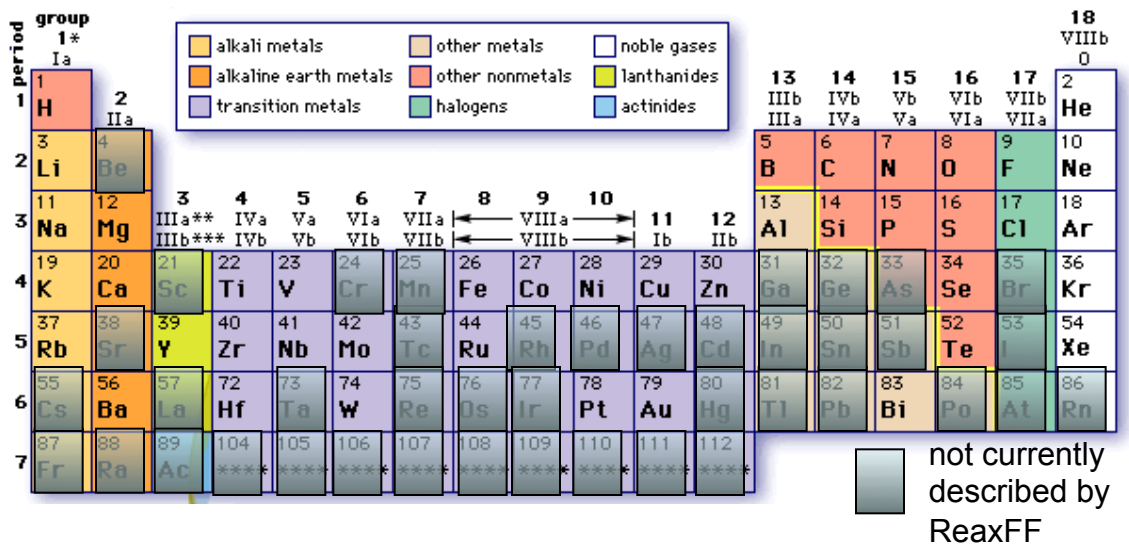


-ReaxFF allows for reactive MD-simulations on systems containing more than 1000 atoms
- ReaxFF is 10-50 times slower than non-reactive force fields
- Better scaling than QM-methods (NlogN for ReaxFF, N^3 (at best) for QM

Current development status of ReaxFF

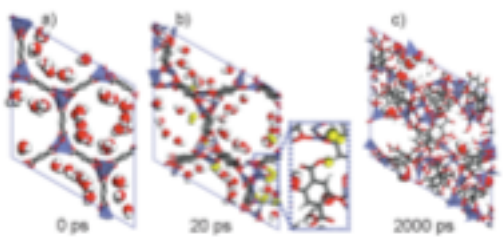
- ReaxFF combines covalent, metallic and ionic elements allowing applications all across the periodic table
- All ReaxFF descriptions use the same potential functions, enabling application to interfaces between different material types
- Code has been distributed to over 150 research groups
- Parallel ReaxFF (LAMMPS/ReaxFF) available as open-source
- Incorporation in ADF/BAND graphical user interface underway

ReaxFF transferability



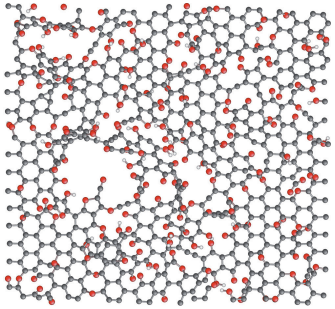
ReaxFF user community

Name	Institute	Distribution date	Application
Adam Skelton	vanderBilt U.	June 2009	Silica/water
Aidan Thompson	Sandia National Lab	July 2005	Incorporation into GRASP
Albert To	U. Pittsburgh	March 2009	Al_2O_3-phase change
Alejandro Strachan	Purdue U.	August 2005	Ferroelectrics, Si-nanowires
Alexey Kaledin	Emory University	June 2010	POM's, FF development
Alexandre Foisy-Geoffroy	CERMM	March 2010	Zeolites
Alister Page	Newcastle U., Australia	July 2008	Methane combustion
Alfonso Pedone	Modena U., Italy	July 2008	SiO_2/water
Andreas Heyden	South Carolina U.	May 2009	Pt/O/H systems
Ana Maria Marin	Universitate Nac. de Columbia	October 2007	Pt/methanol
Ananth Grama	Purdue U.	May 2007	Software development
Andreia Luisa da Rosa	U. Bremen	June 2009	Zn/O/water
Antonio Cammarata	U. Palermo, Italy	Feb 2009	Y/H/BaZrO3
Alvo Aabloo	U. Uppsala, Sweden	May 2007	Polymers, fuel cells
Art Cho	U. Korea	February 2008	Protein/metal
Ioana Cozmuta	NASA/AMES	May 2006	N/O impact on cerami
Anatoly Belonoshko	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
Brian Heinz	ARL, Maryland	August 2008	Ni/Al; Ni/O
Blas Pedro Uberuga	Los Alamos National Lab	June 2004	PAH-clusters
Angela Violi	U. Utah	April 2003	PAH-clusters
Camilo Calderon	U. Boston	November 2009	Gold
Catherine Tweedie	MIT	May 2007	Polymer surfaces
Chansoo Kim	Korea	April 2009	PDMS/Ar
Christian Ciobanu	Colorado School of Mines	June 2009	Silicon carbides
Chris Pickard	St. Andrews, Scotland	October 2007	Method development
Christine Wu	LLNL	June 2010	TATB/Estane
Christopher Strickland	Pacific Northwest National Lab	April 2007	H_2-storage
Chun-Wei Pao	Los Alamos National Lab	September 2009	Ni/S failure
Daniel Curelle-Ferre	Total, Clean Coal	November 2009	Combustion/CO_2 captu
Daniel Friese	U. Bremen, Germany	April 2007	Radiation damage
Dmitry Bedrov	U. Utah	March 2007	Alumina/graphite
Donald Phelps	Air Force Research Labs	September 2006	Polymer/Nickel
Dongshen Wang	University of London	September 2008	Al-oxidation
Doug Doren	U. Delaware	July 2007	Cu ions in water
Eduardo Bringa	Livermore National Labs	May 2006	Li/C/H systems
Chunguang Tang	U. Connecticut	June 2008	Hf/Si/O systems
Elodie Salmon	IFP, France	February 2006	Kerogen cracking
Erik Santiso	NC State U.	February 2004	Hydrocarbons
Ferdaus Faruq	NC State	June 2010	Nanodiamond collisio
Fang Chen	Sichuan University, China	May 2010	CNT/H-storage
Francesco Ferrante	U. Palermo	November 2009	Organic fluids
Fidel Valega	Delft University of Tech.	January 2010	Cu/hydrocarbons
John Daily	U. Colorado	June 2008	Cellulose
Feng Ding	Rice University	July 2007	CNT growth on Ni
Feng Wang	U. Boston	June 2010	Water
Joel Fried	U.Dayton	August 2010	Phosphates
R.J.M. Konings	Inst.for TransU, Germany	May 2006	Uraniumnitride
Florent Calvo	Lab. Phys.Quant. France	August 2005	Si/SiO clusters
Gerrit Groenhof	Max Planck Goetingen	April 2010	DNA polymerases
German Samolyuk	Oak Ridge National Lab	June 2010	Fe/W metal

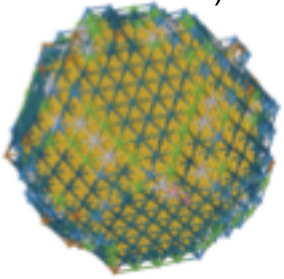


MOF stability under water loading
(Han et al., ChemComm 2010)

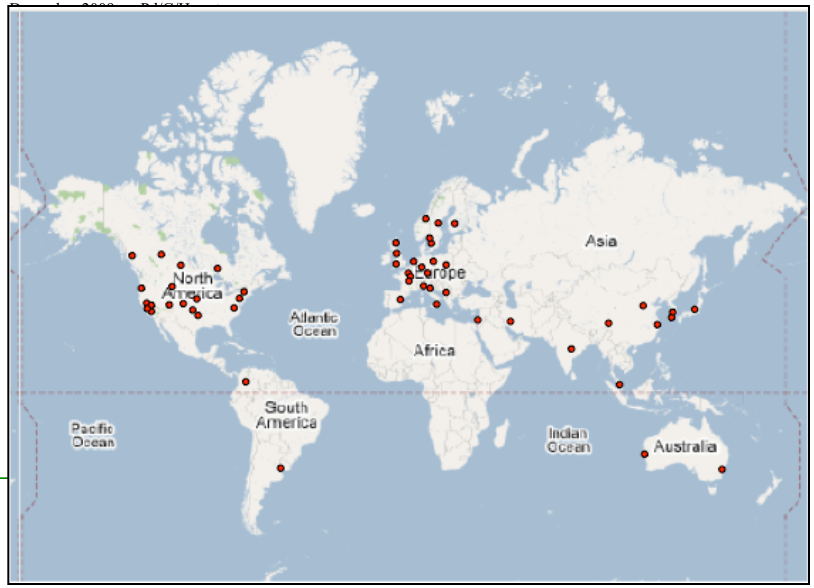
Luzheng Zhang	U. New Mexico	May 2007	Ti/TiO; HE-materials
Mahmoud Abu-Samha	U. Bergen, Norway	November 2007	Water clusters
Magnus Bergh	FOI Sweden	May 2010	Hydrocarbon oxidation
Marcela Bilek	U.Sidney, Australia	June 2009	Protein/PE interface
Marcelo Flores	UNICAMP, Brazil	December 2008	Nanowires, all-carbon
Markus Buehler	MIT	August 2005	Crack propagation
Matt LaBrosse	U. Pittsburgh	June 2006	W/Co/C
Manuel Louwerse	TNO Defense, NL	July 2008	HE-materials
Micael Baudin	U. Uppsala. Sweden	October 2005	Zn/ZnO
Michael Marsella	UC Riverside, CA	July 2010	Proteins
Milan Oncek	Prague Inst. Of Chem. Techn.	January 2010	Pt/H Oniom
Mike Salazar	Union University	January 2007	Force field development
Nicholas Winter	Livermore National Lab.	August 2004	High-energy materials
Norbert Lümmen	University of Bergen, Norway	July 2008	High-temperature methane
Olivier Politano	Inst. Carnot de Bourgogne	August 2009	Ni/water systems
Paul Kent	ORNL	February 2010	Carbon/Li interactions
Paul Mikulski	US Naval Academy	May 2005	Amorphous carbon
Philippe Sautet	ENS Lyon	October 2007	Ni/hydrocarbons
Poonam Doiphode	Inst. For Plasma Res. India	February 2005	Hydrocarbons
Ram Devanathan	Pacific Northwest National Lab	August 2007	Proton transfer/TiO_2
Remedios Cortese	U. Palermo	October 2009	Zn/MOF
Renee van Ginhoven	Sandia National Labs.	February 2005	Si/SiO_2 interfaces
Riad Manaa	LLNL	June 2010	Fluorohydrocarbons
Rob Riggleman	U. Madison	August 2004	Organosilicates
Rosa Bulo	Free University of Amsterdam	January 2010	Protein/water
Rick Muller	Sandia National Labs.	January 2004	Software development
Rui Zhu	U. Calgary	April 2007	Proteins
Ruth Pachter	AFRL	October 2009	Au/S/C/H interactions
Rutuparna Narulkar	Oklahoma State	August 2008	Si/diamond impact
Sae-Jin Kim	KIST, Korea	February 2008	Si/O/H systems
Samir Mushrif	McGill U., Canada		
Sangsoo Han	KAIST, Korea		
Sangsoo Han	KRISS, Korea		
Scott Dunham	U. Washington		
Scott Habershon	U.Oxford, UK		
Sean Nedd	Iowa State U.		
Chan Hay Yee Serene	Nanying Tech. Singapore		
Sergio Calvo	Texas A&M		
Silvia Nedea	TU Eindhoven, Holland		
Song Charng	Iowa State		
Sophya Garashchuk	U. South Carolina		
Stan van Gisbergen	SCM (ADF/BAND)		
Philippe Simonetti	CEA, France		
Samira Gholani	U. Isfahan, Iran		
Sofia Akber	Scripps Institute		
Sonia Tulyani	U. Massachusetts		
Thomas Schoenfelder	TU Chemitz		
Tom Schwartzentruber	U. Minnesota		
Takumi Hawa	NIST		
Tahir Cagin	TexasA&M		
Tengfei Luo	MIT		
Thomas Kraska	U. Koeln, Germany		
Thuat Trinh	TU Eindhoven, Holland		
Tim Germann	Los Alamos National Labs.		



Graphene oxidation
(Bagri et al., Nature Chem. 2010)

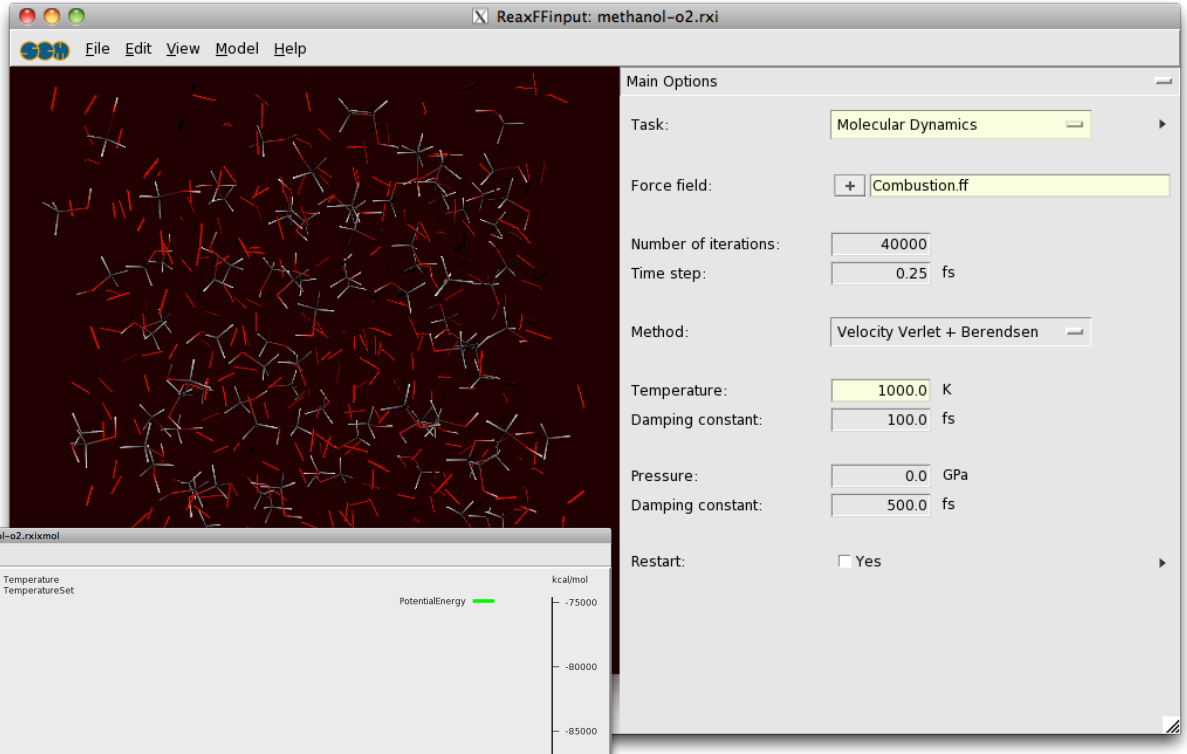


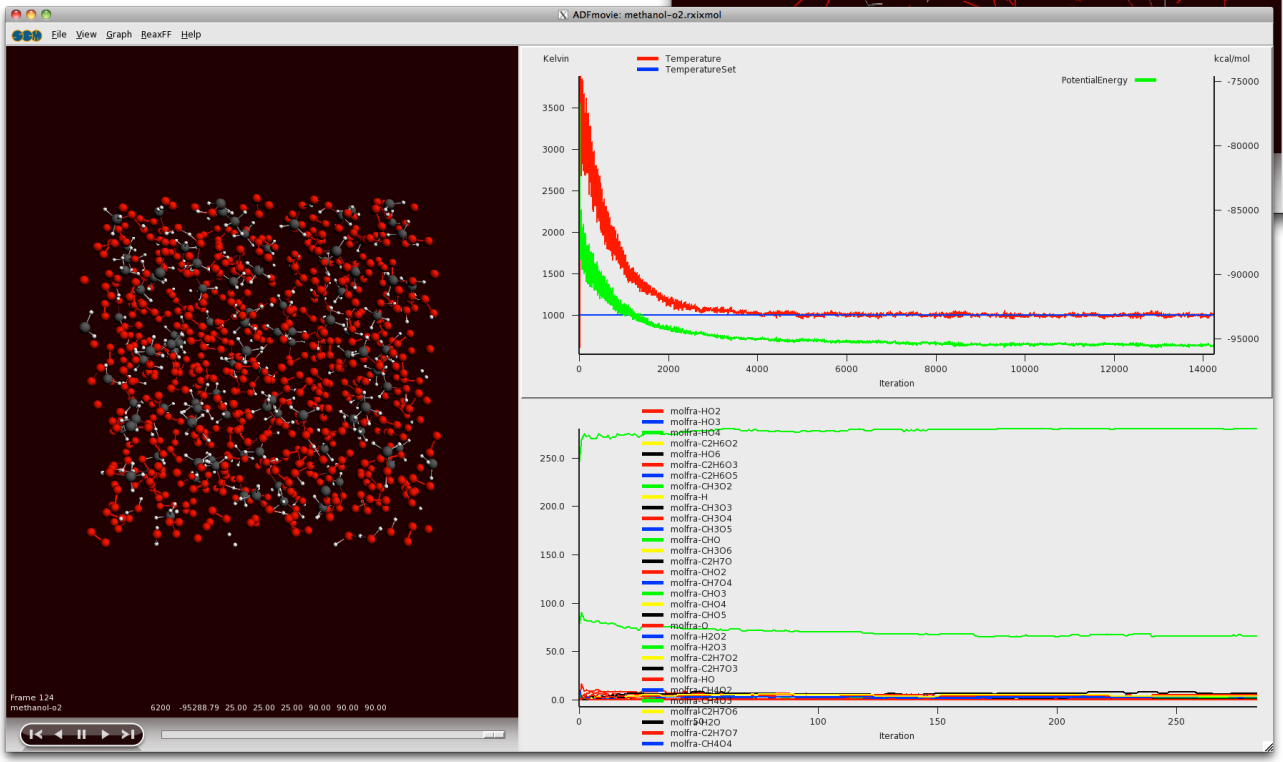
Annealing of gold nanoparticles
(Keith et al., PRB 2010)



ReaxFF integration into ADF/BAND graphical user interface

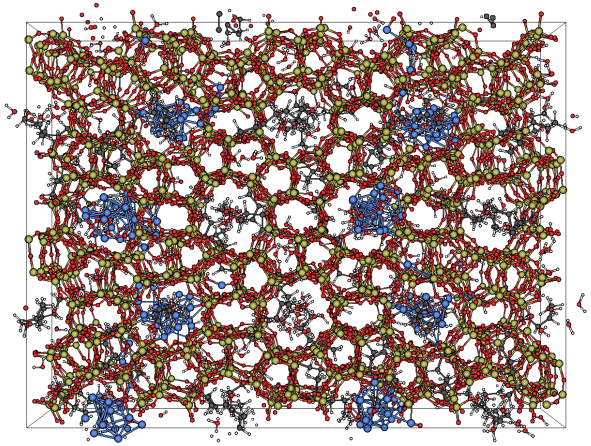
- Collaboration with SCM.
- Professional software support team.
- Beta-version GUI available
- Parallel version + code optimization planned.
- Direct integration of state-of-the art DFT/FF/TB codes.



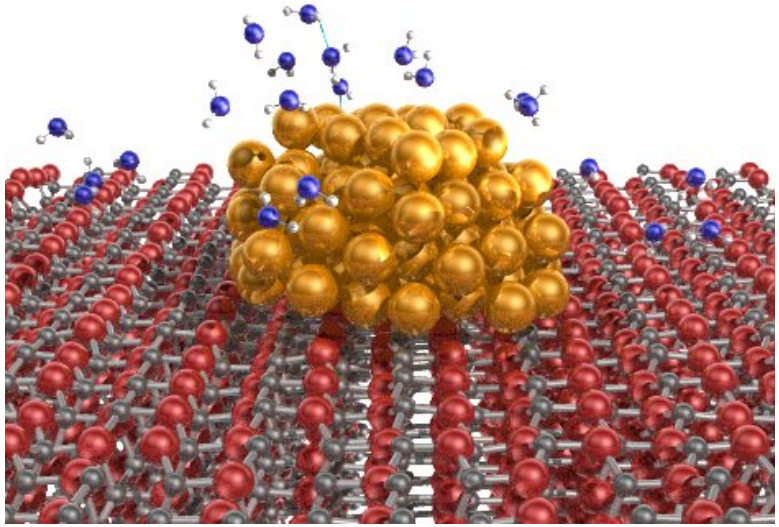


Integration team:
- Stan van Gisbergen, Olivier Visser, Alexei Yakovlev (SCM)
- Mike Russo, Kaushik Joshi (Penn State)

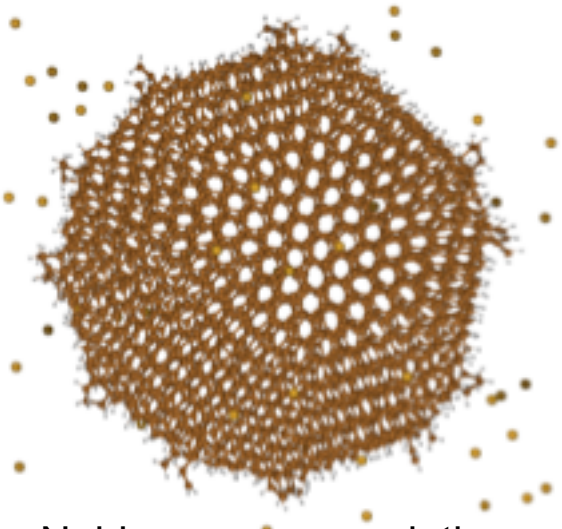
Examples of recent LAMMPS and ADF/ReaxFF simulations



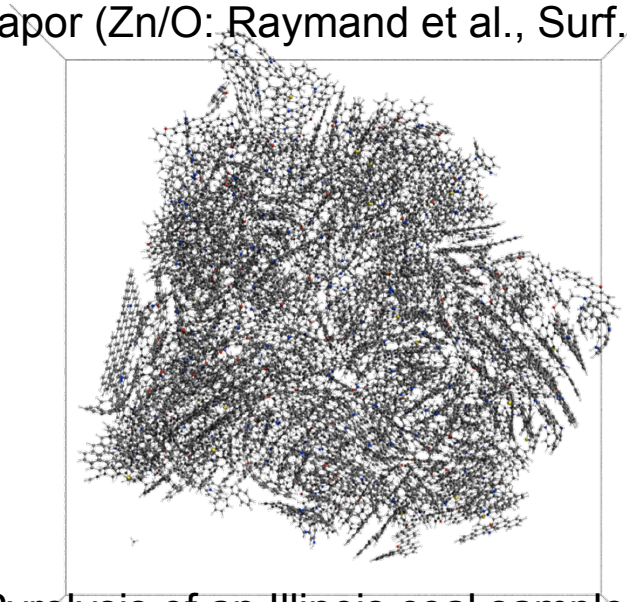
Hexane cracking on a Fe/H-ZSM5 catalyst (Fe/O: Aryanpour et al., JPC-A 2010)



Cu-metal particle on a ZnO-support with water vapor (Zn/O: Raymand et al., Surf. Sci. 2010)



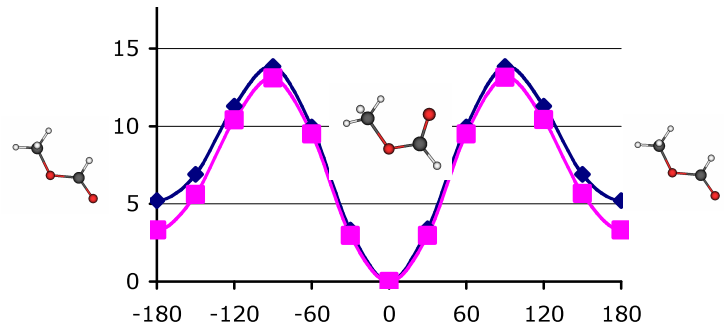
Noble gas accomodation coefficients on a graphene wafer (Kamat et al., submitted to JPC-A)



Pyrolysis of an Illinois coal sample (Kamat, Russo, Mathews and van Duin, in preparation)

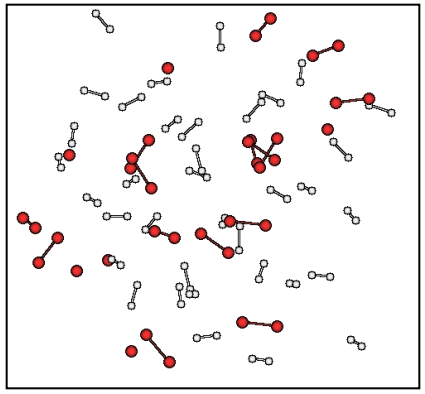
Combustion reactions

QM



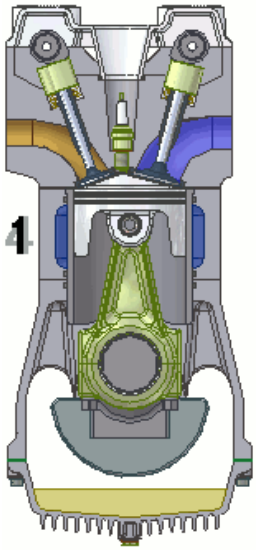
- Accurate energies for key reaction paths
- Size range: up to around 100 atoms
- Mostly static, highly limited dynamics

ReaxFF



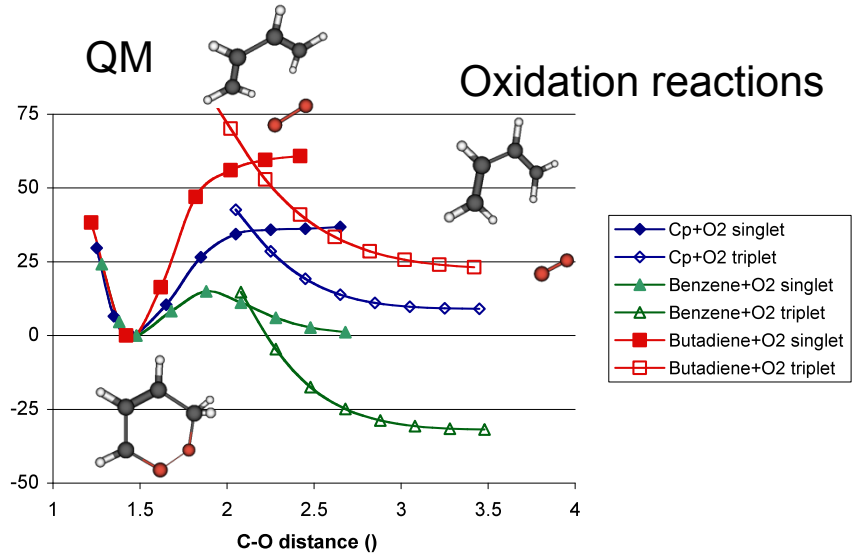
- Allows nanosecond-dynamics for systems up to 10^7 atoms
- Can be parameterized directly from QM

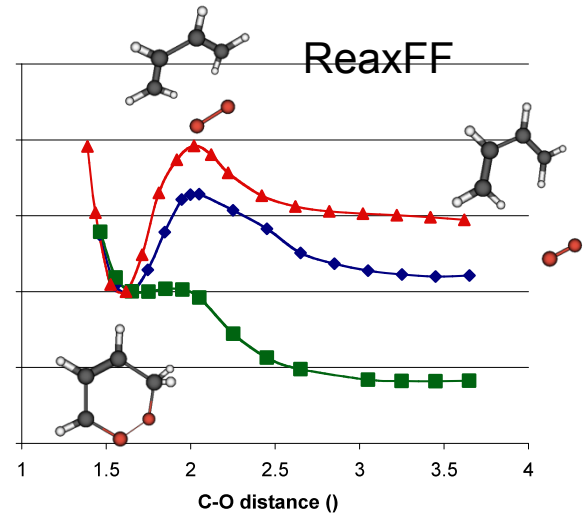
Engineering



Database of reaction kinetics and diffusion constants

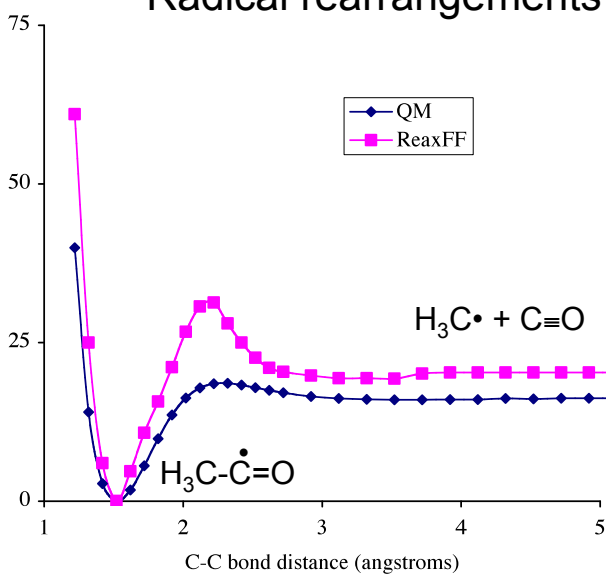
Force field development: hydrocarbon oxidation



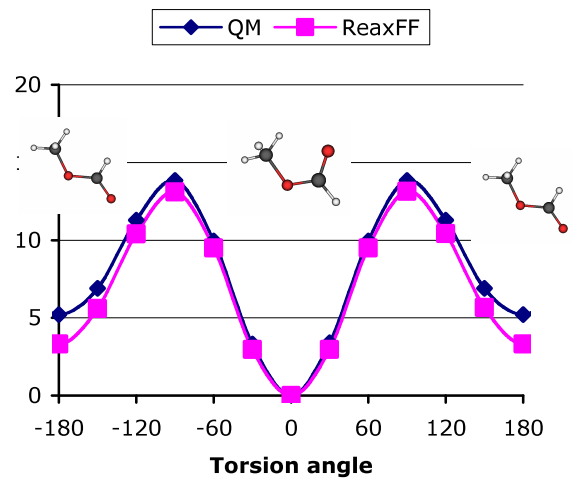


QM: Jaguar/DFT/B3LYP/6-311G**

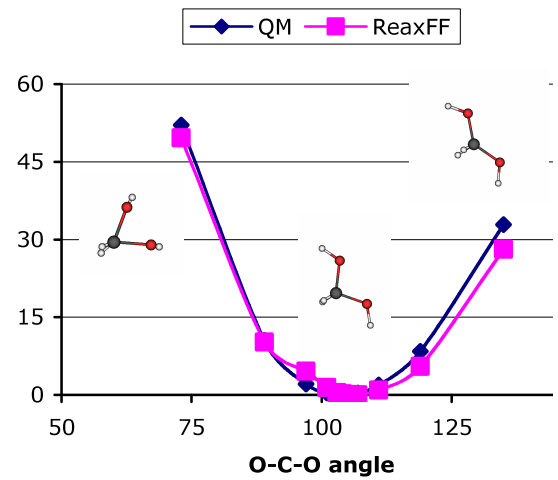
Radical rearrangements



Rotational barriers

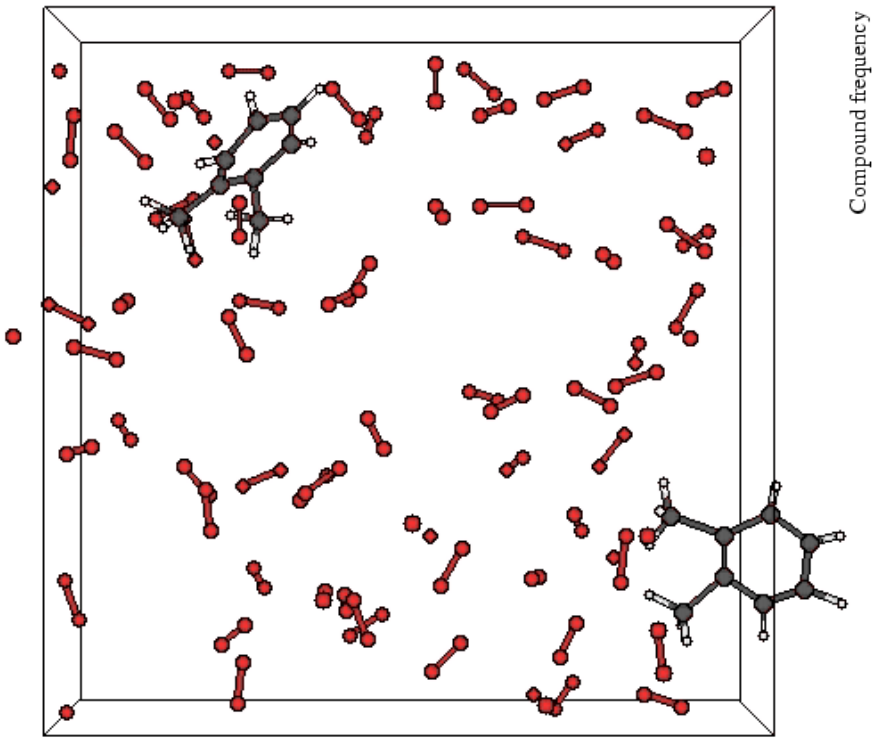


Angle strain

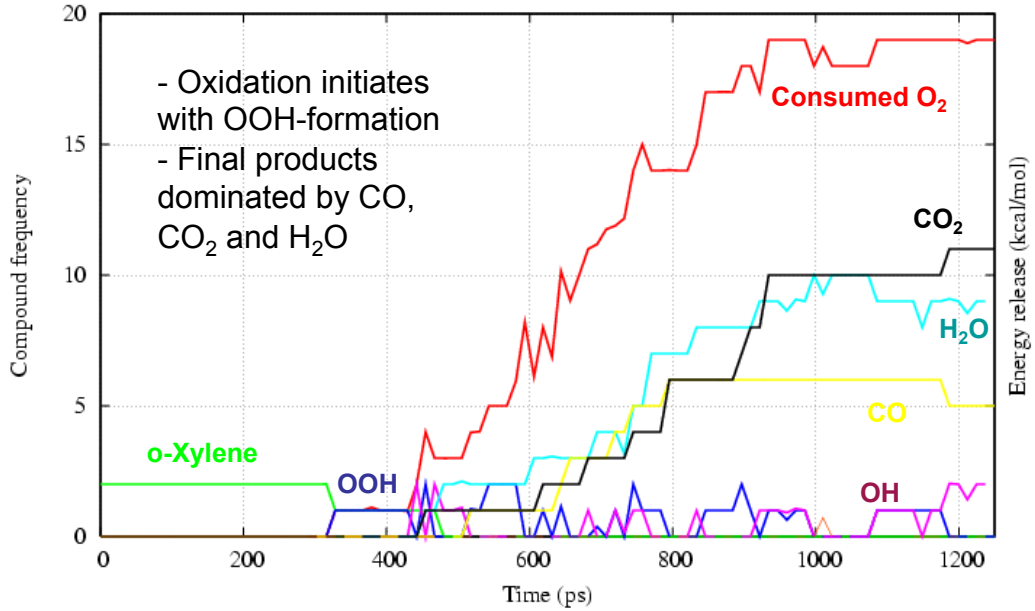


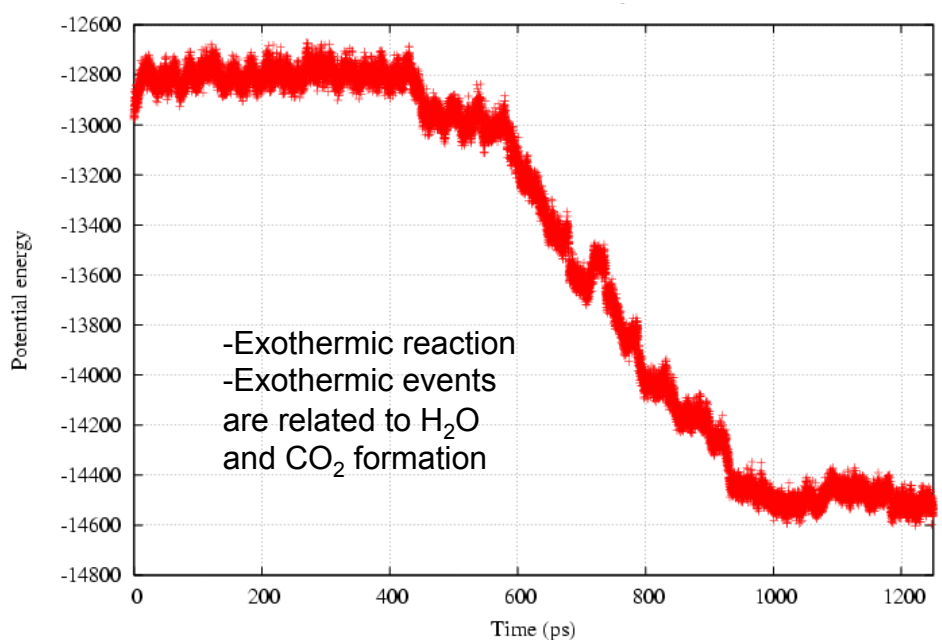
- total training set contains about 1700 compounds

Test ReaxFF CHO-description: oxidation of o-xylene



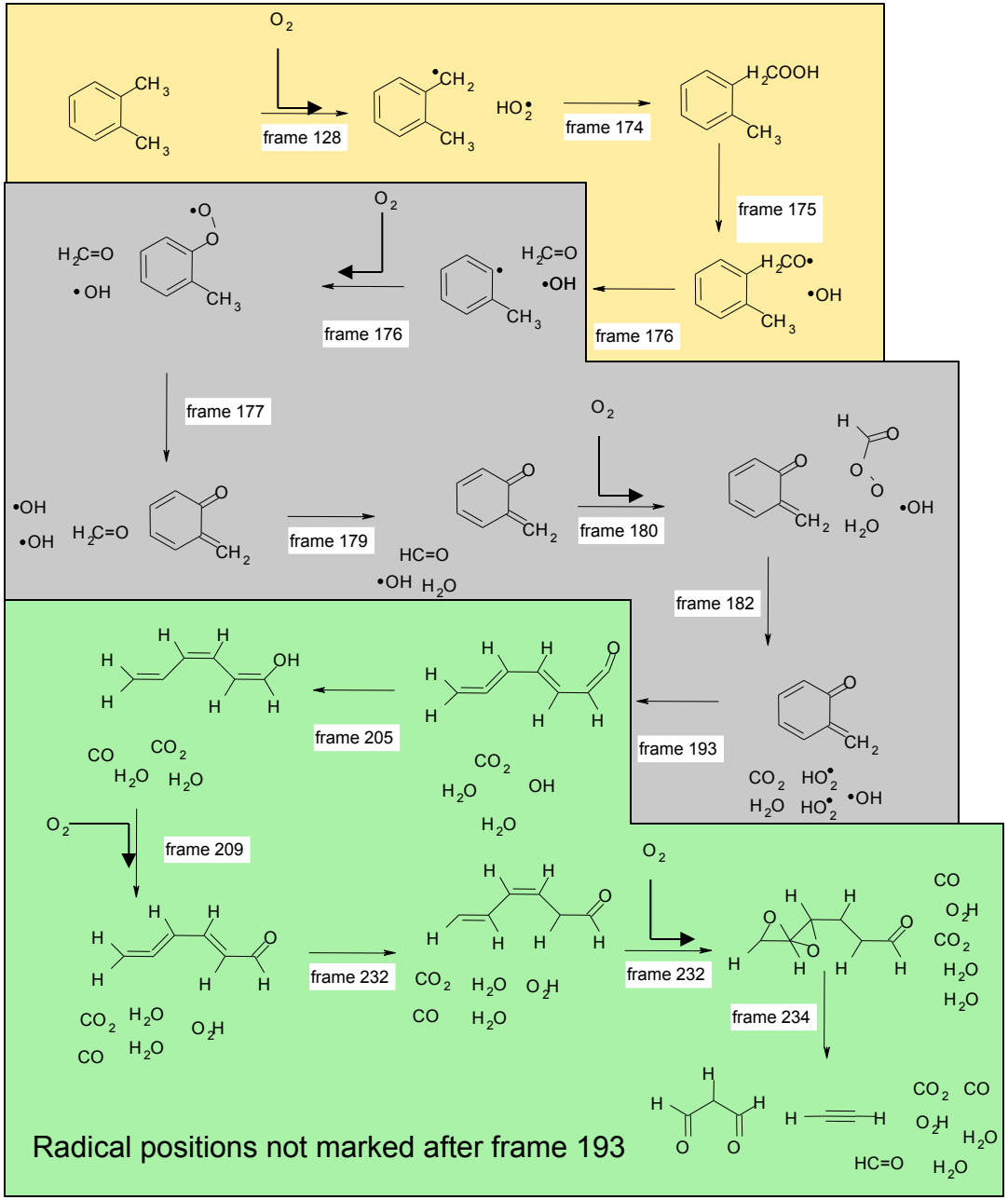
2 o-Xylene; 70 O_2 in 20x20x20 Angstrom box
ReaxFF NVT/MD at T=2500K





Chenoweth, van Duin and Goddard, JPC-A 2008

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

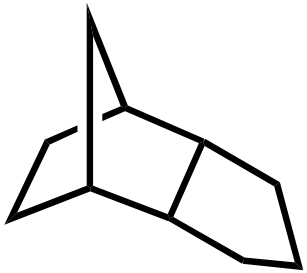
- Ring opens shortly after destruction of aromatic system

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

-ReaxFF gives sensible predictions for the o-Xylene oxidation mechanism.
- This mechanism can be further validated against QM

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

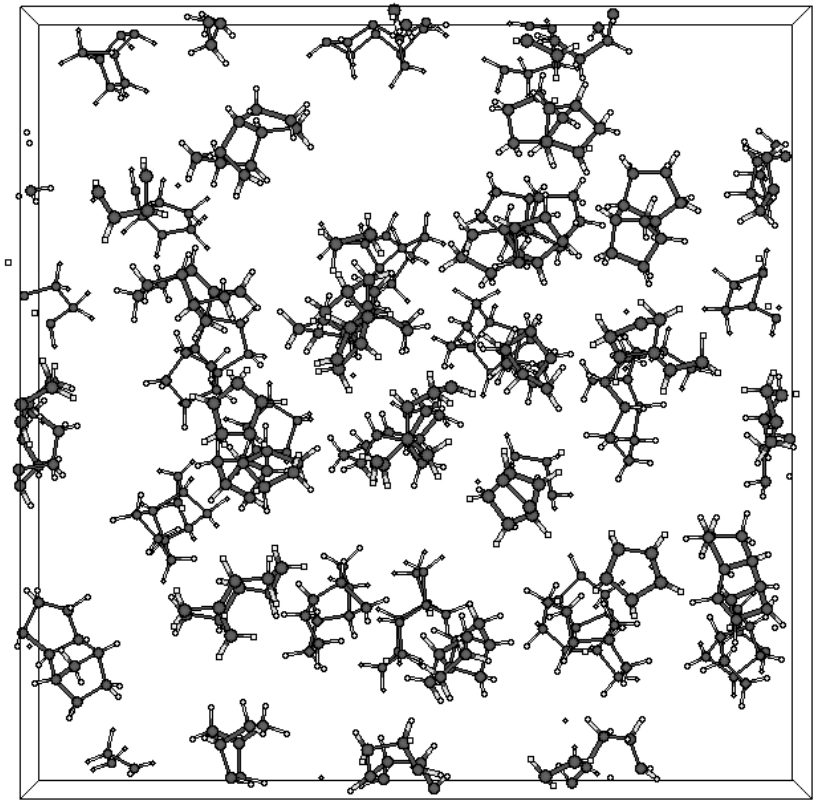
with Kimberly Chenoweth, Siddharth Dasgupta and Bill Goddard (Caltech)



Exo-tetrahydrodicyclopentadiene: JP-10

- **Synthetic high-energy density fuel**
  - Volumetric heat content: 39434 MJ/m^3 (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

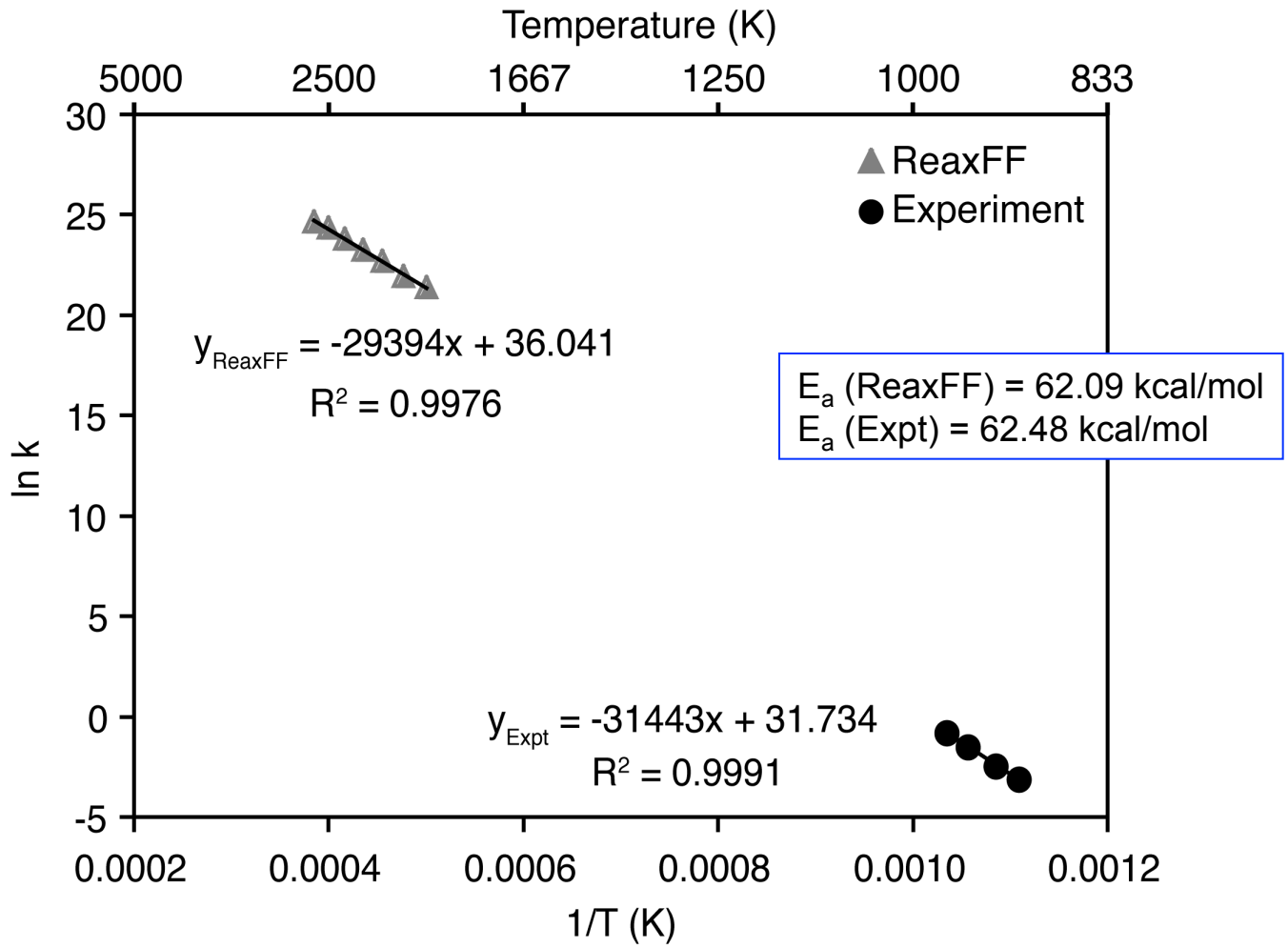


- **40 JP-10 Molecules (1040 atoms)**
- **Density = 0.388 g/cm^3**
- Equilibrated at 1500K for 10 ps
- Temperature control using Berendsen thermostat with 0.1 ps damping constant
- MD time step of 0.1 fs
- **Total simulation time: 50 ps**

•Perform a series of NVT-MD simulations to calculate activation energy and product distribution

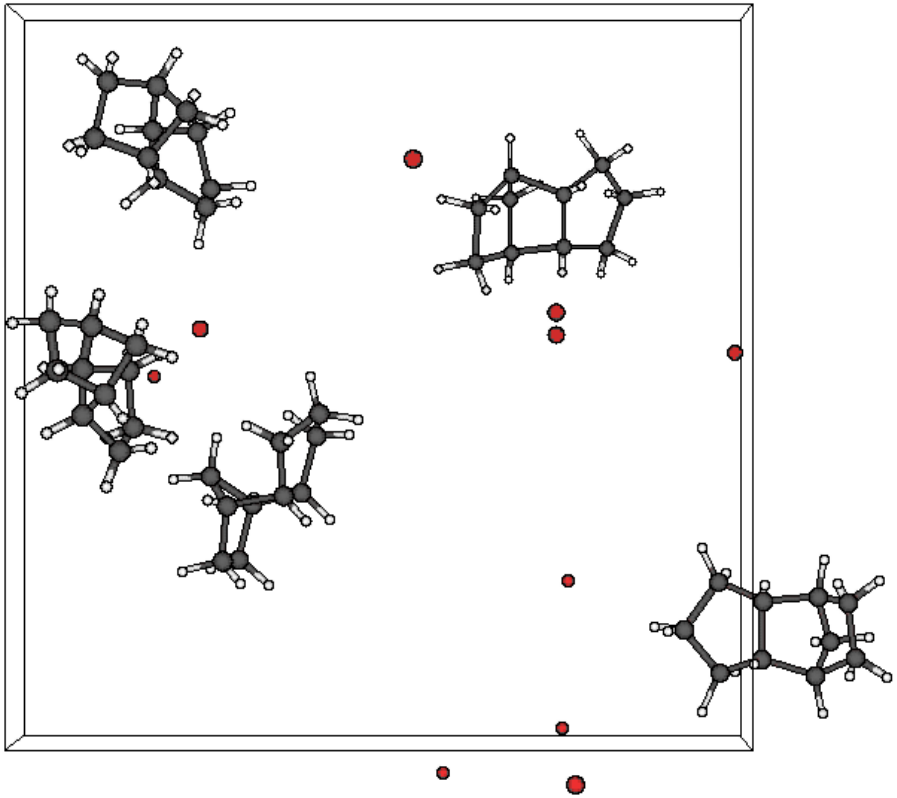
- **Temperature (K): 2000, 2100, 2200, 2300, 2400, 2500, 2600**
- 10 simulations at each temperature with unique starting configuration
- Results obtained by averaging over the 10 simulations at each temperature

Kinetics for JP-10 Pyrolysis



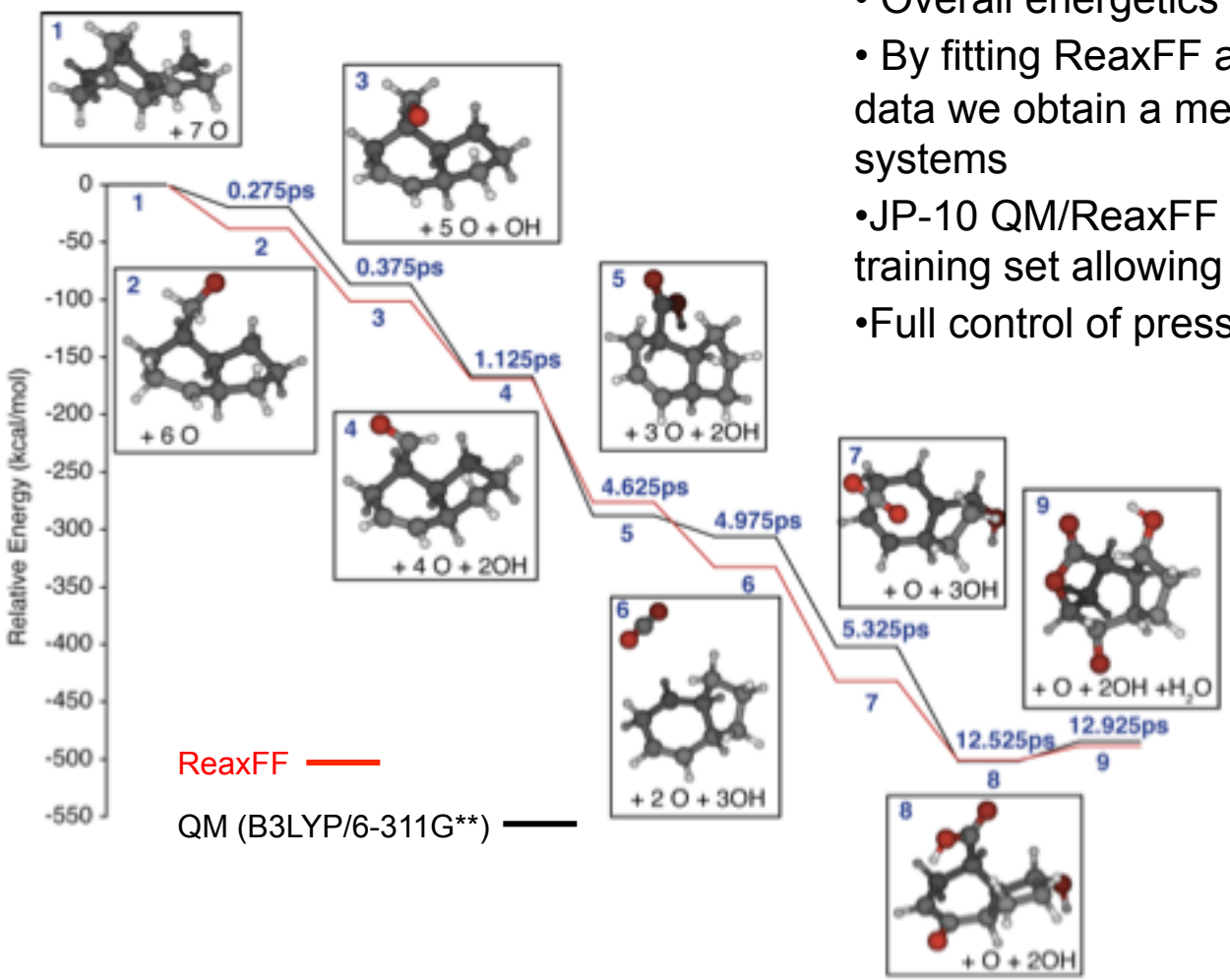
- Excellent agreement with experiment (Rao and Kunzru, J. Anal. Appl. Pyrolysis 2006)

Simulation strategy for JP-10 oxidation



- **5 JP-10 molecules**
- **10 oxygen radicals**
- 140 atoms
- Density = 0.174 g/cm^3
- 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



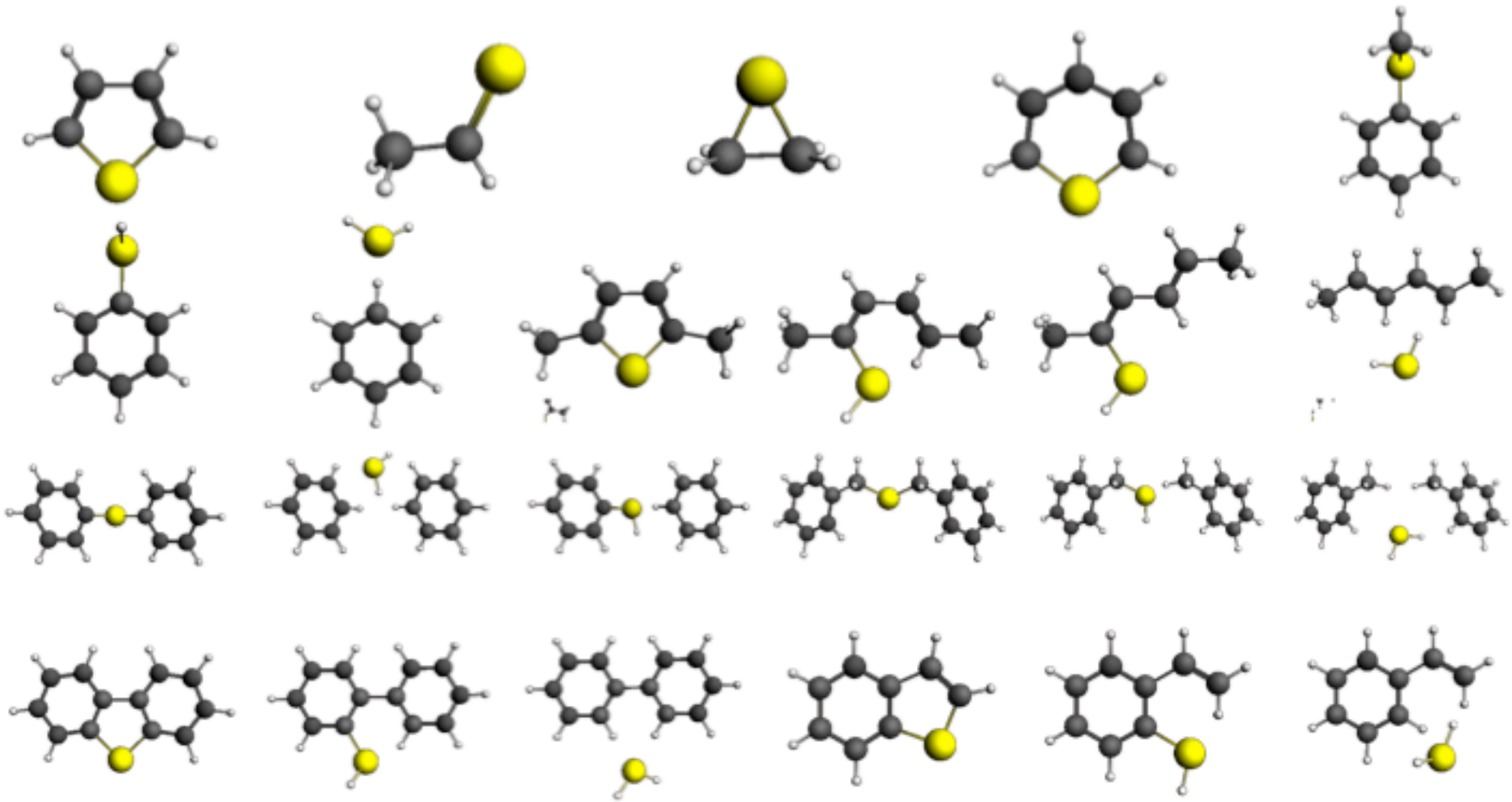
- Reaction mechanism observed during NVT-MD simulation at 1000K
- Overall energetics in good agreement with QM
- By fitting ReaxFF against a large database of QM-data we obtain a method that is transferable to new systems
- JP-10 QM/ReaxFF comparison can be fed back into training set allowing the force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

Chenoweth, van Duin, Dasgupta and Goddard, J.Phys.Chem.A 2009

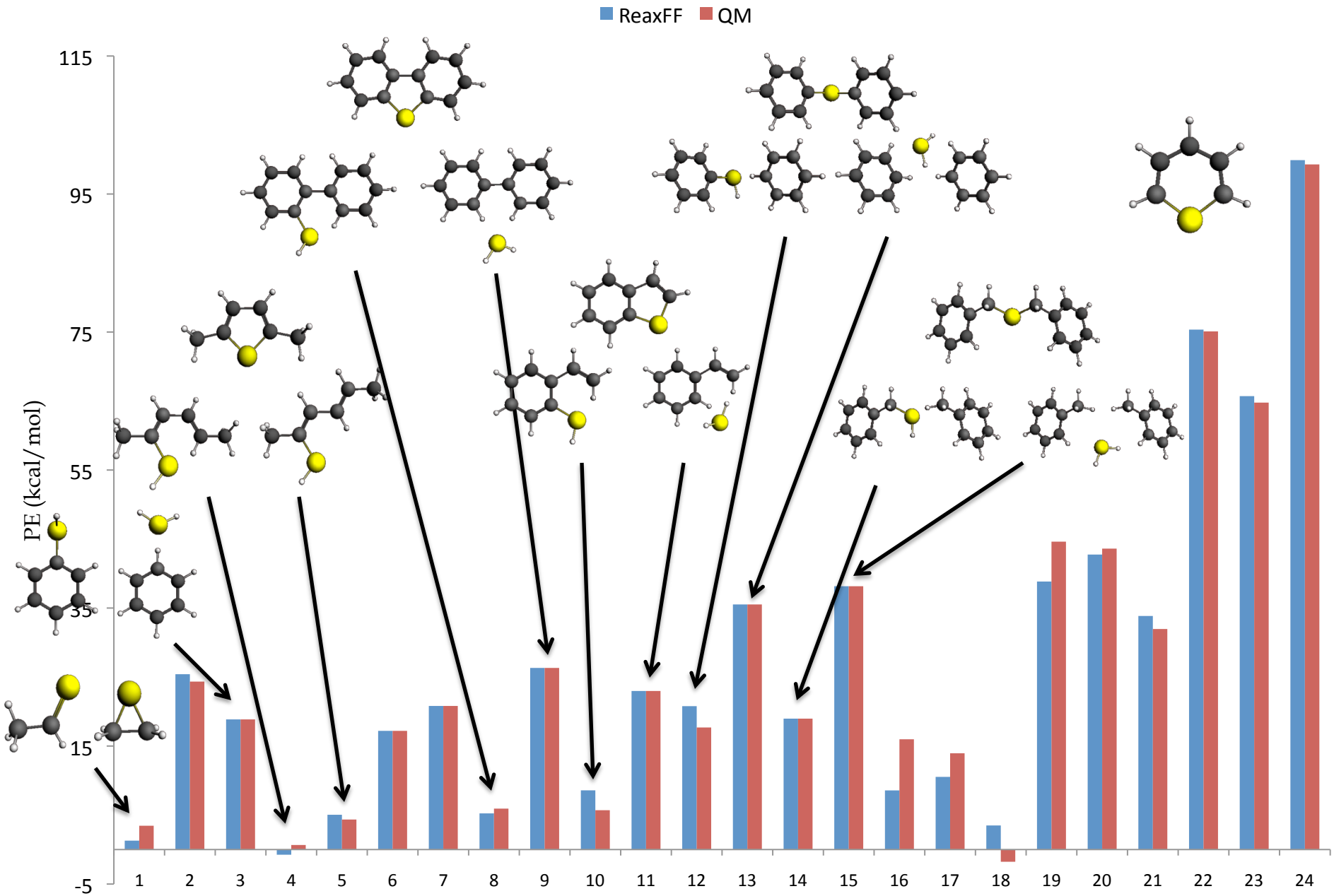
Extension to sulfur chemistry with applications to coal pyrolysis

With Mike Russo, Amar Kamat, Fidel Castro and Jonathan Mathews

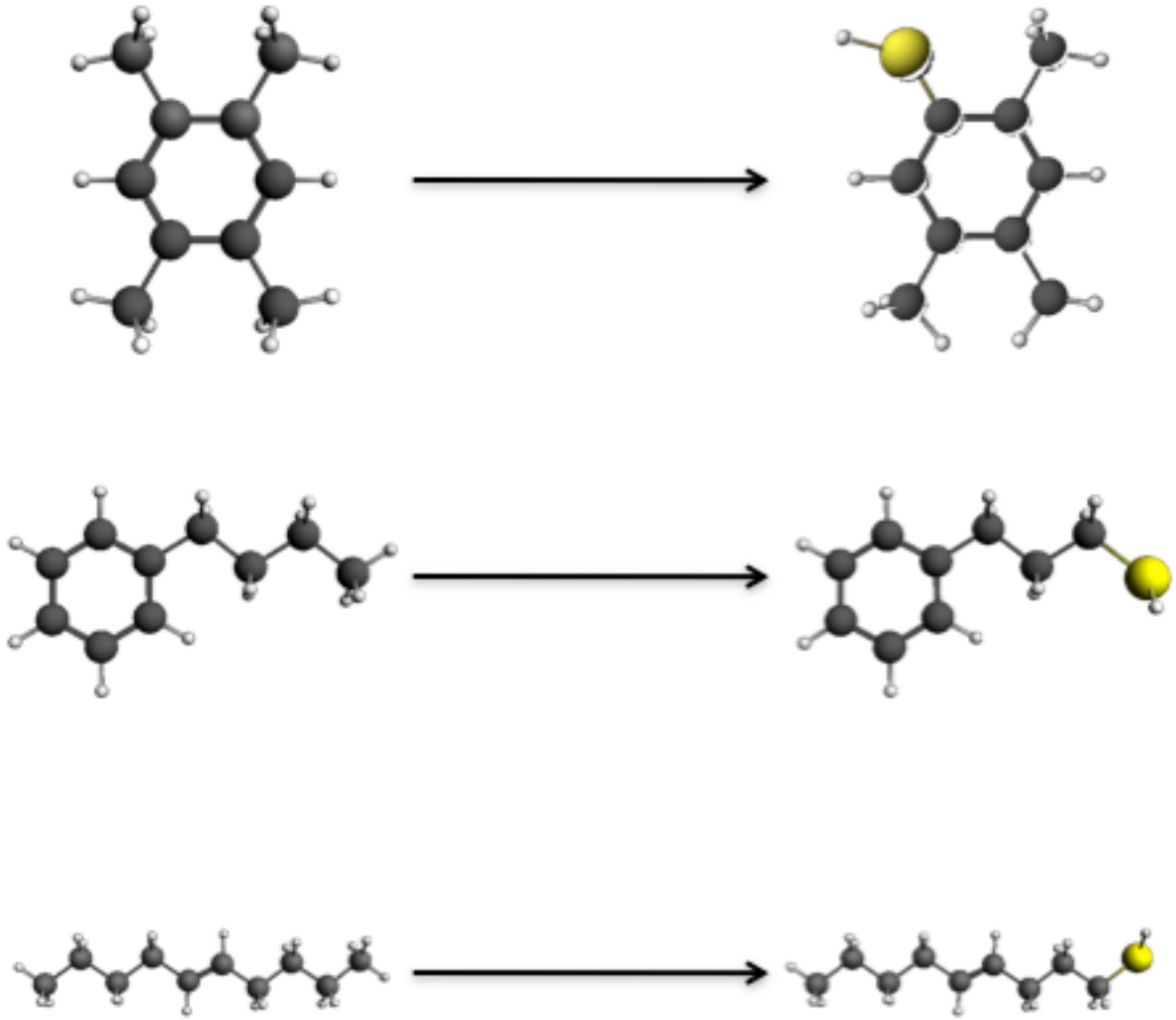
Compounds included in the training set



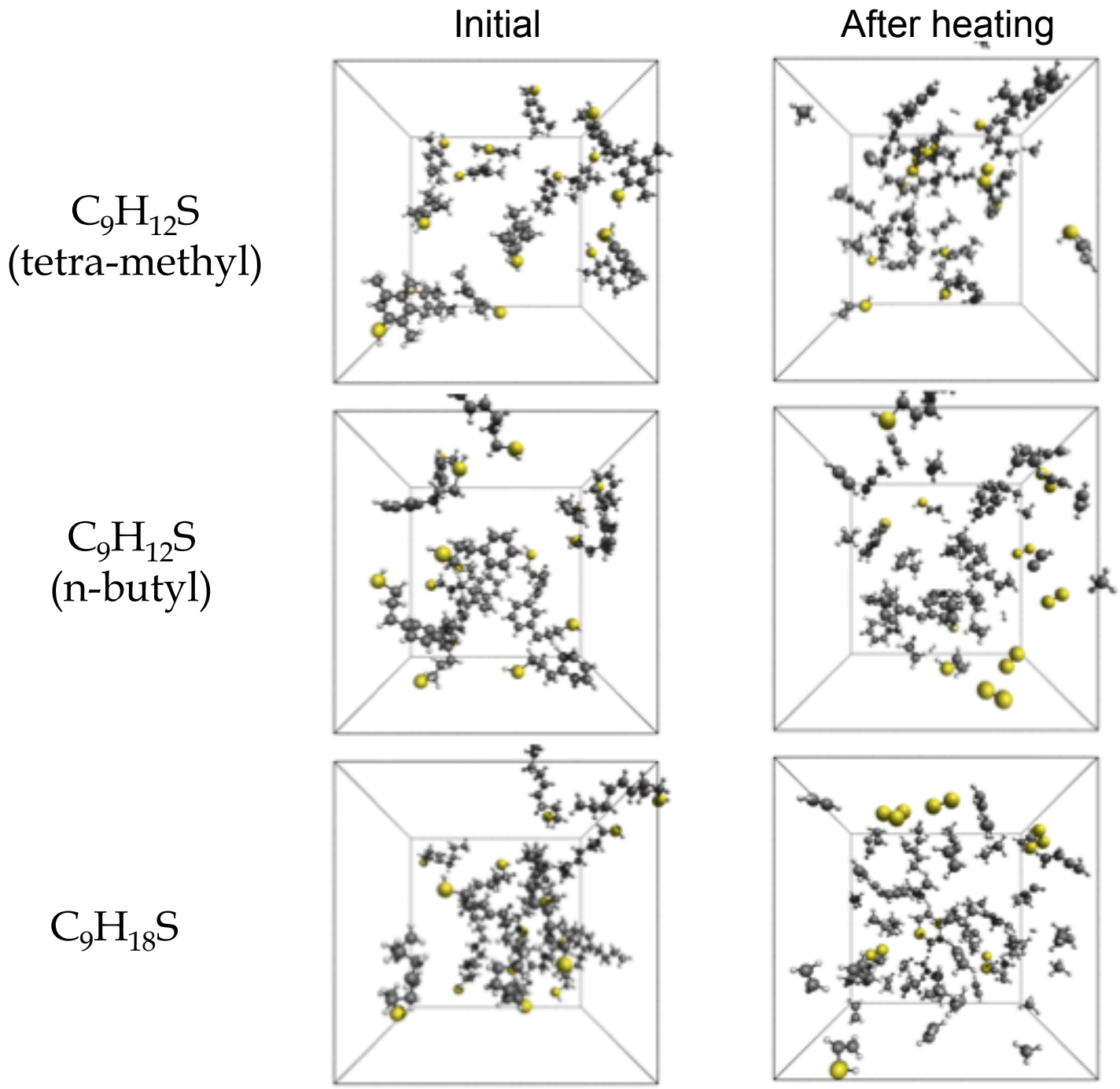
Hydrogenation energies

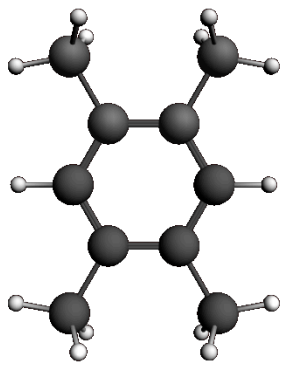


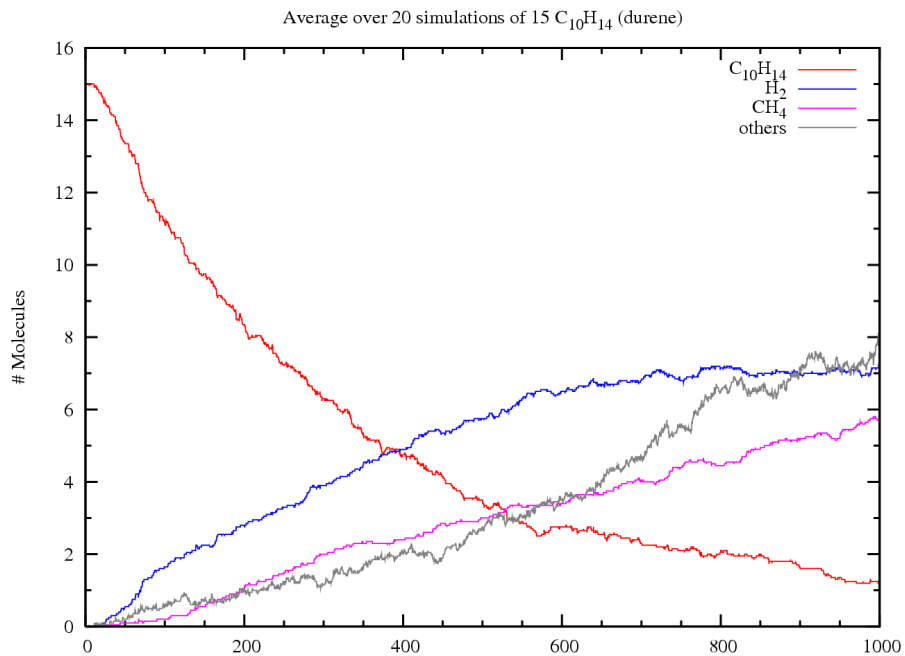
Sulfur Effects on pyrolysis

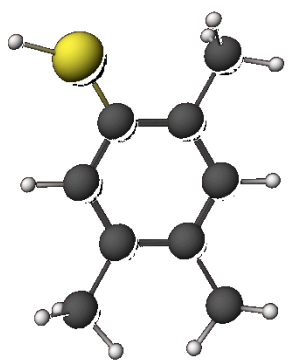


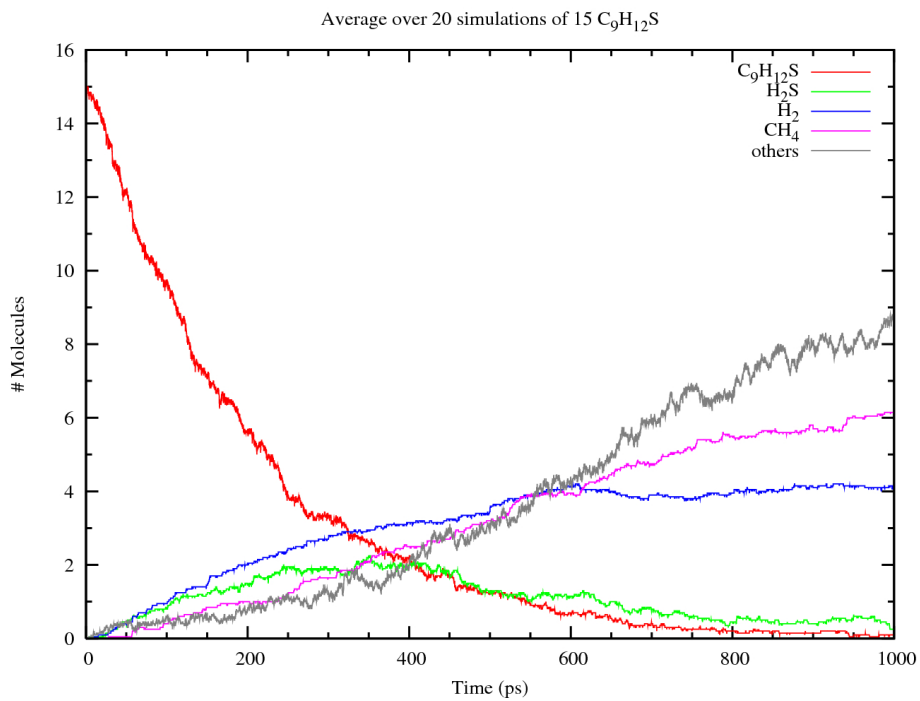
- Examine the initiation differences caused by the sulfur:
  - Rate/time
  - Init. step
  - Intermediate and final products
  - Lifetime of aromatics


Initial
After heating
$C_9H_{12}S$
(tetra-methyl)
$C_9H_{12}S$
(n-butyl)
$C_9H_{18}S$



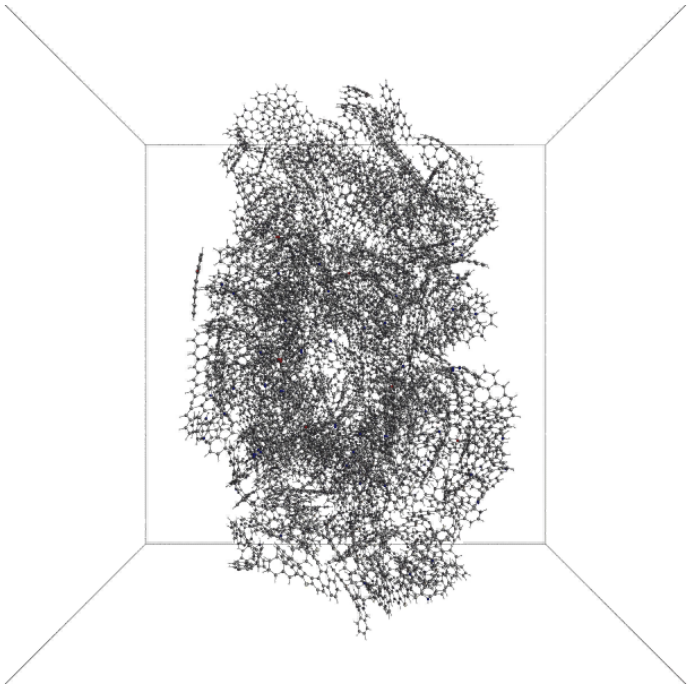




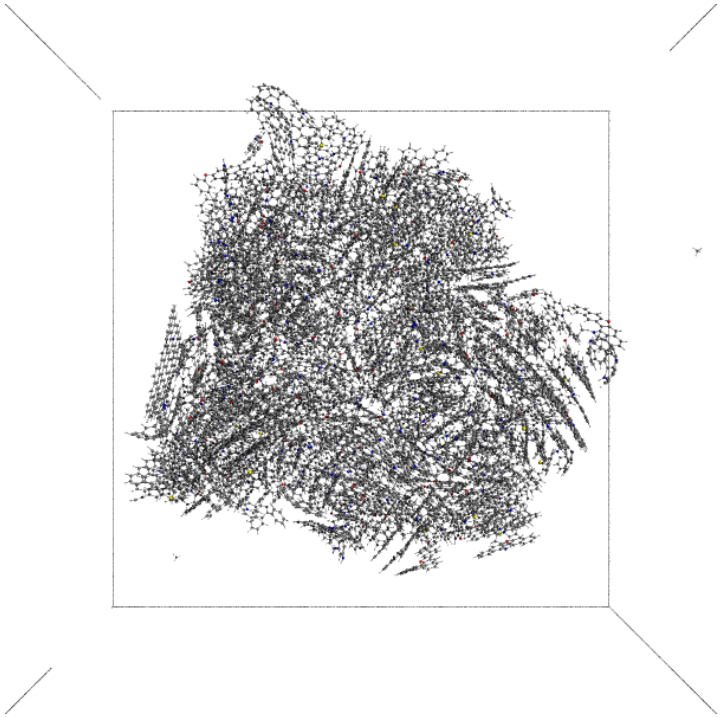


- Sulfur substitution significantly speeds up reaction kinetics

Initial application to coal pyrolysis



Coal structure, 20,000 atoms
C:S ratio: 100:1, from Fringe3D [1]

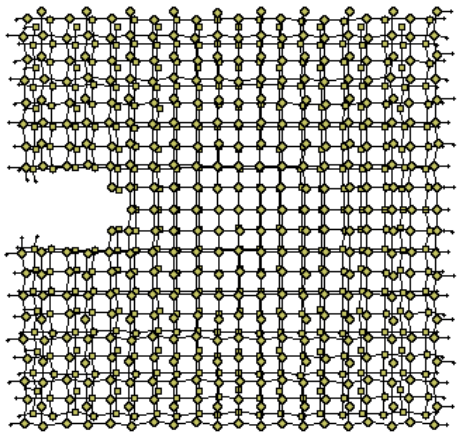


MD simulation with
temperature ramp

[1] Ferdandez-Alos, V., J.K. Watson, and J.P. Mathews. *Directly capturing aromatic structural features in coal via "Fringe3D" generating 3D molecular models directly from HRTEM lattice fringe images*. in *Prepr. Pap.-Am. Chem. Soc., Div. Fuel Chem.* 2009. Salt Lake City, UT.

Outline

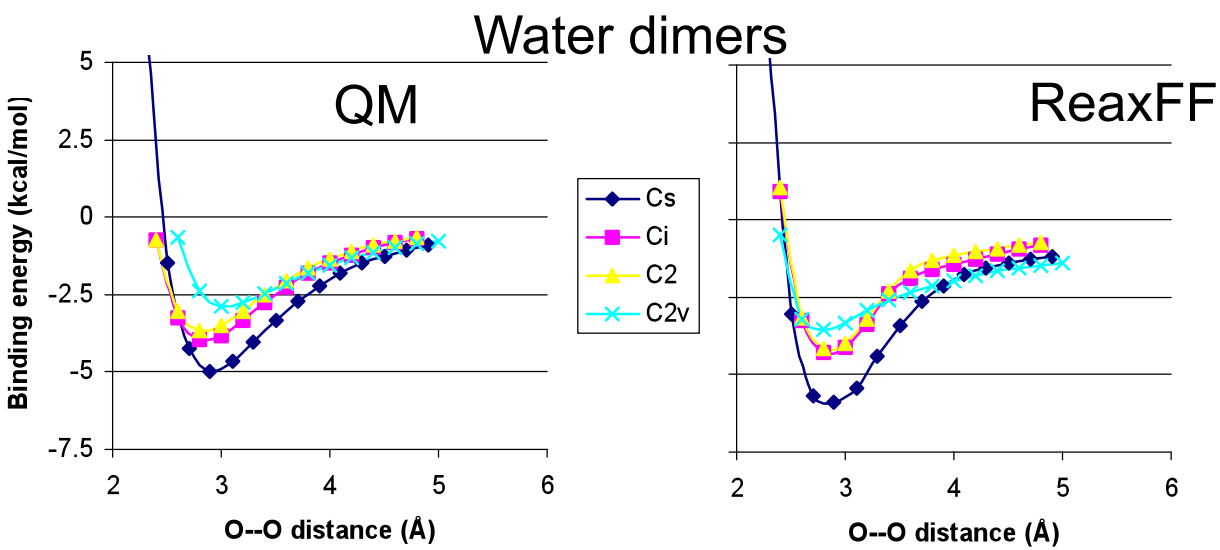
- Simulations on the dynamics of chemical reactions
- The ReaxFF reactive force field
- Overview of ReaxFF applications
    - Combustion reactions
    - **Material failure**
    - Catalysis
- Summary

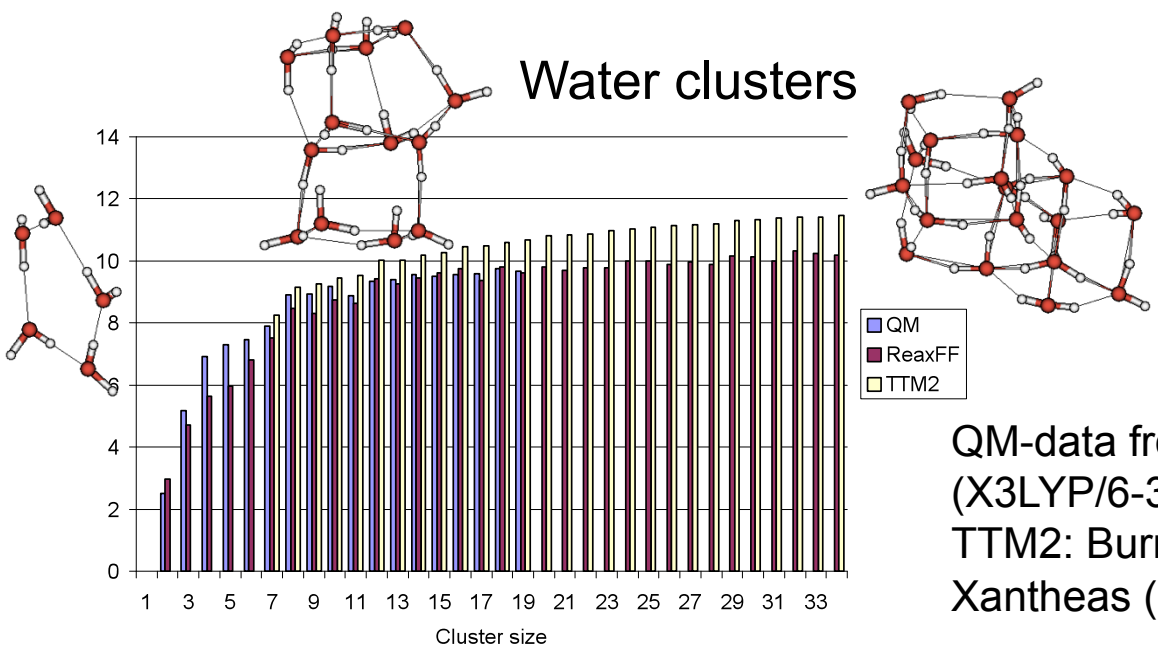


ReaxFF simulation on crack propagation in silicon

Buehler et al. PRL 2006
Buehler et al., PRL 2007

Aqueous phase chemistry simulations



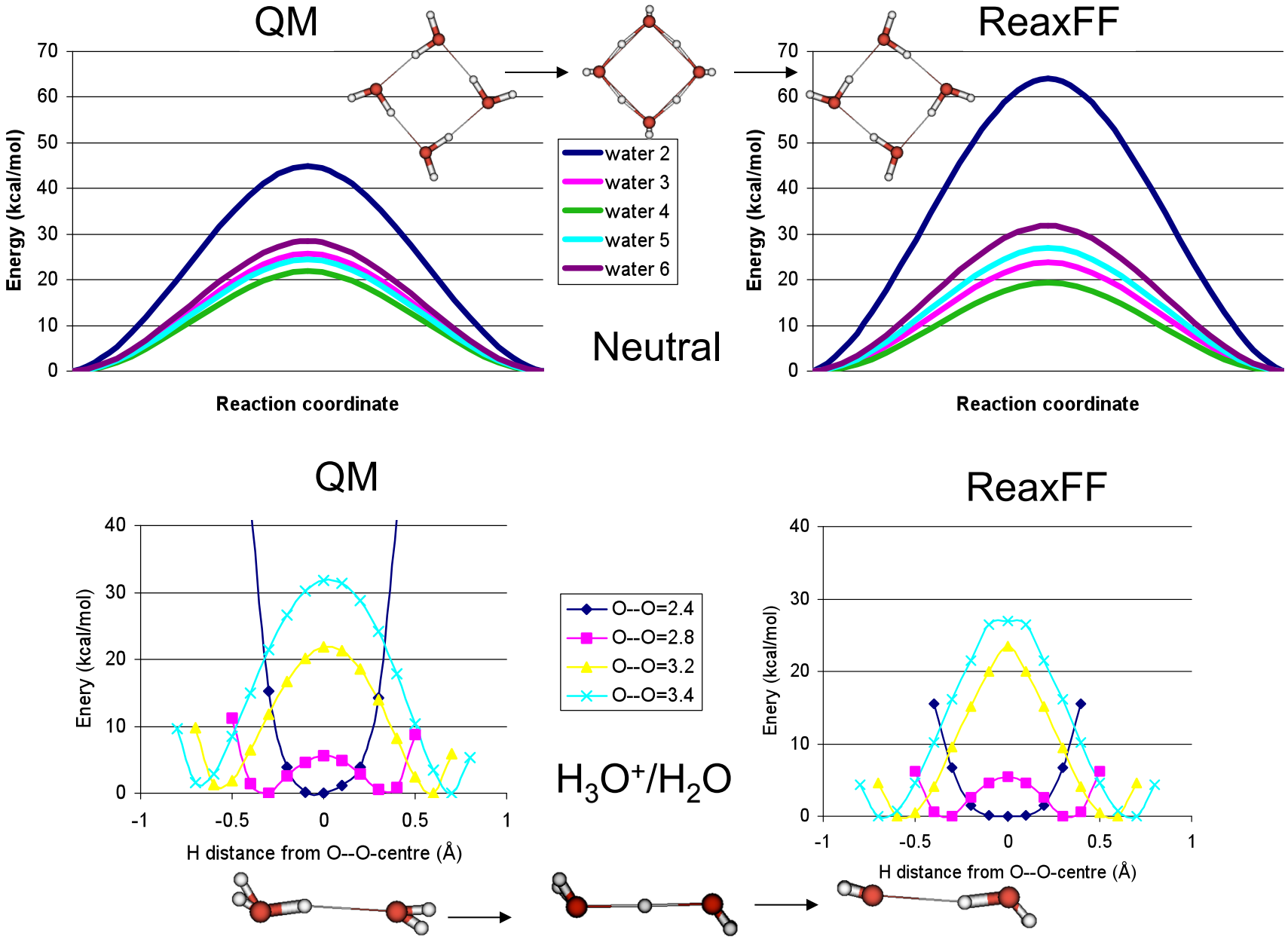


Other data in training set:

-H-O-H bond dissociation
-H-O-H angle disortion
- Ice(cmc) equation of state
- Mulliken charges for water clusters
- Water vibrational frequencies
- H-H, O=O and HO-OH bond dissociation

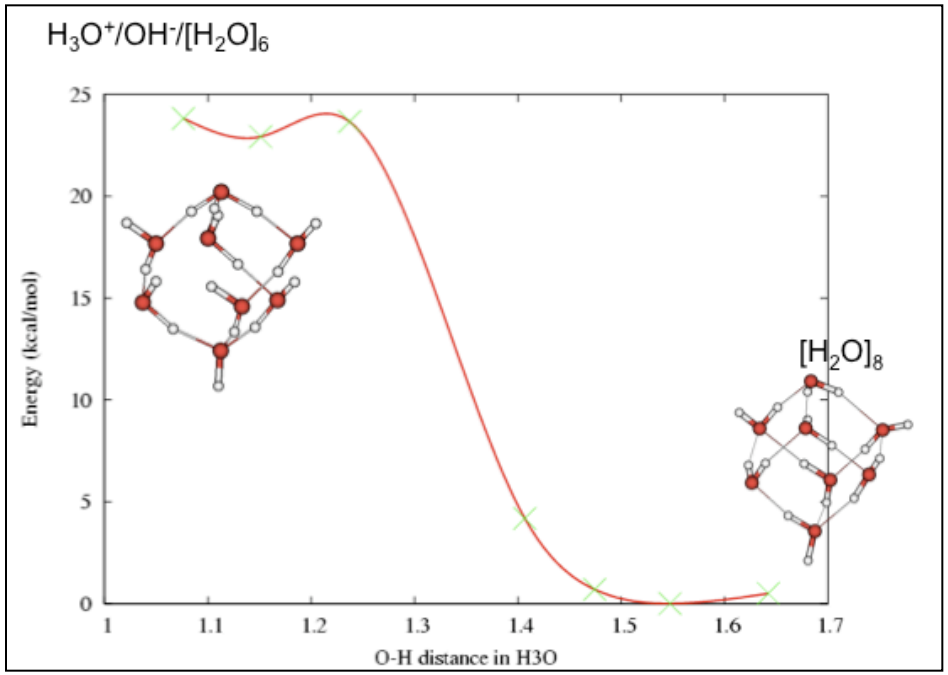
QM-data from Julius Su (X3LYP/6-311G**)
TTM2: Burnham and Xantheas (JCP 2002)

Hydrogen transfer barriers

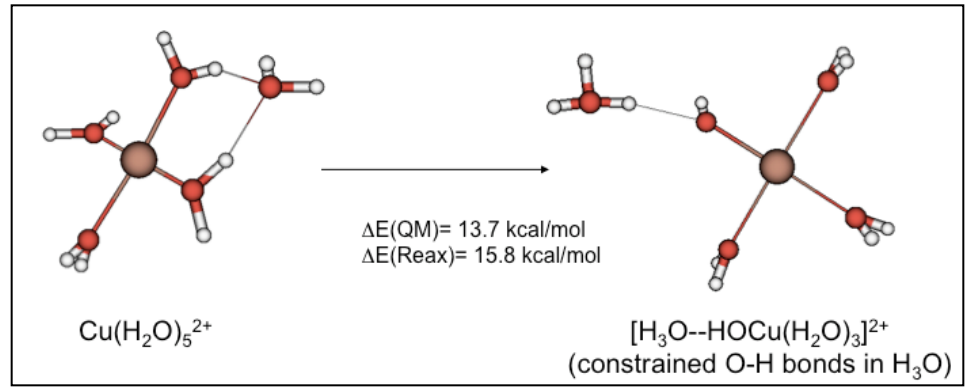


Auto- and Cu-assisted ionization of water

$[H_2O]_8$ cluster



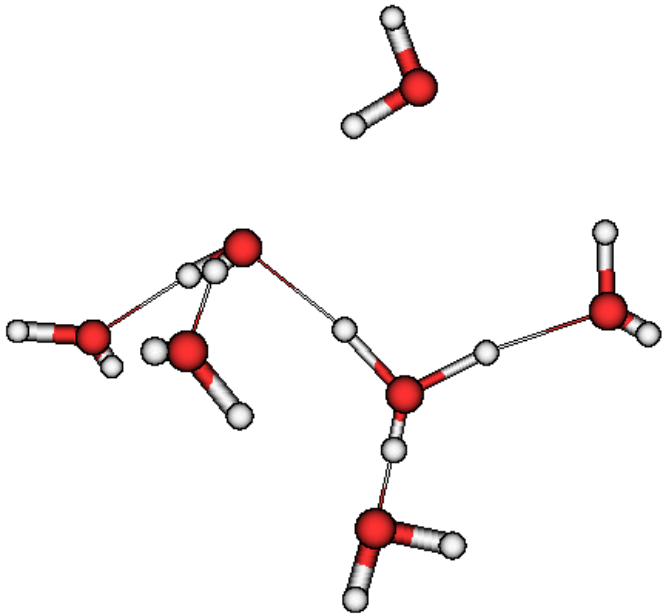
$Cu(H_2O)_5^{2+}$

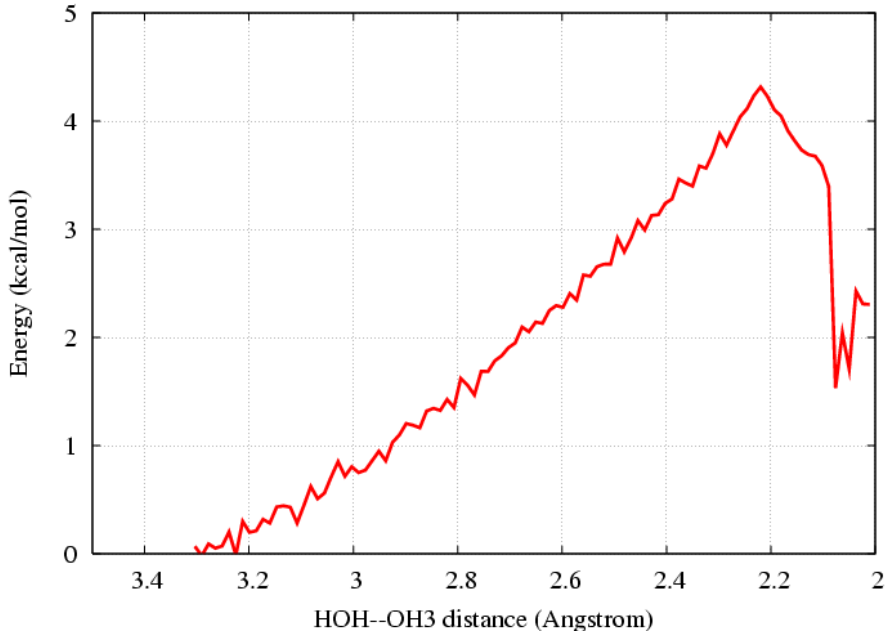


- Good agreement with QM-data (Svozil and Jungwirth, JPC-A 2006; 25.5 kcal/mol; small barrier)

- Cu-ion greatly assists in the ionization of water

Solvation-induced proton transfer

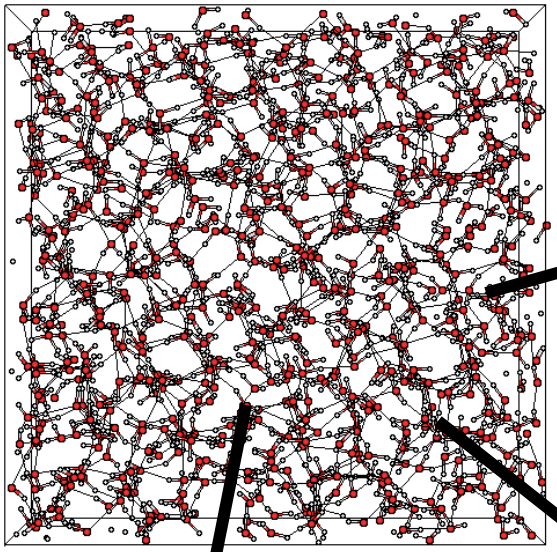




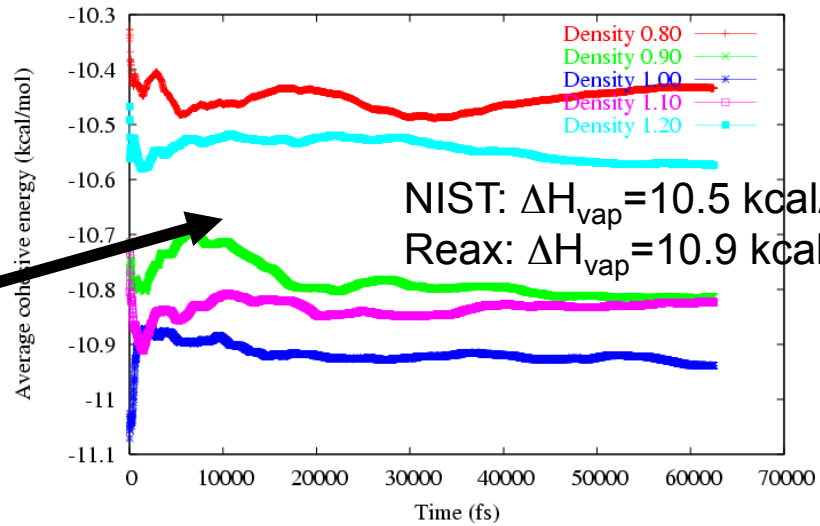
- ReaxFF predicts that a solvation-change can trigger proton transfer

Molecular dynamics tests of ReaxFF for bulk water

800 water box

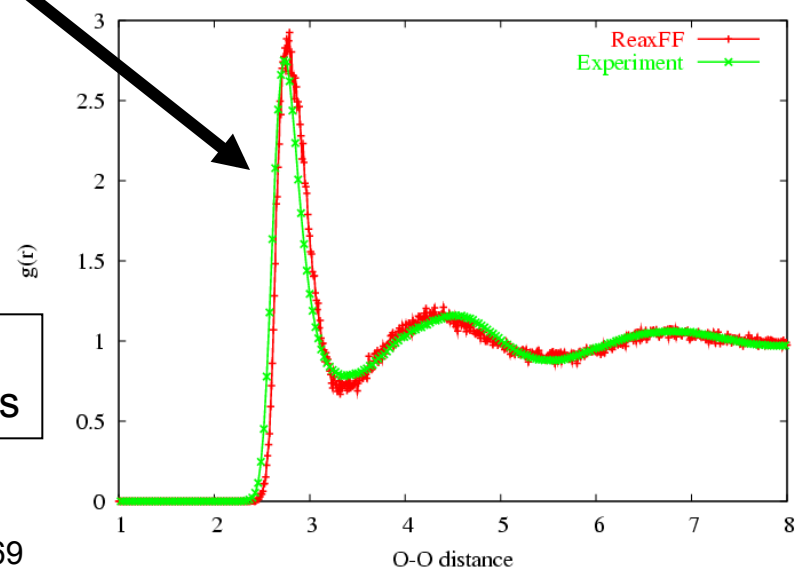


Density, cohesive energy



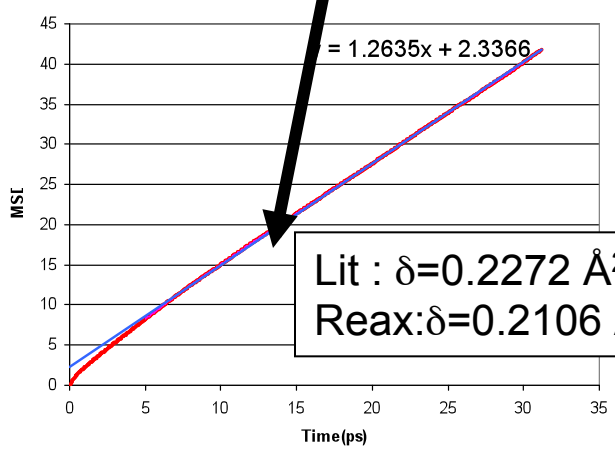
NIST: ΔH_{vap}=10.5 kcal/mol
Reax: ΔH_{vap}=10.9 kcal/mol

Radial distribution



Experimental data from Chem. Phys. Special Issue vol. 258, pp. 121-137 (2000)

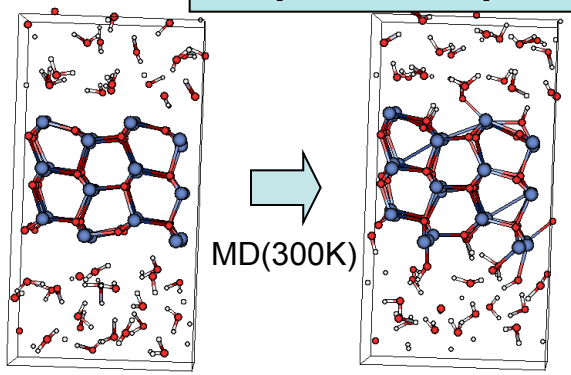
Diffusion constant



Lit : δ=0.2272 Å^2/ps
Reax:δ=0.2106 Å^2/ps

Eisenberg and Kauzman, Oxford Univ. Press 1969

Aqueous phase reactions and surface chemistry

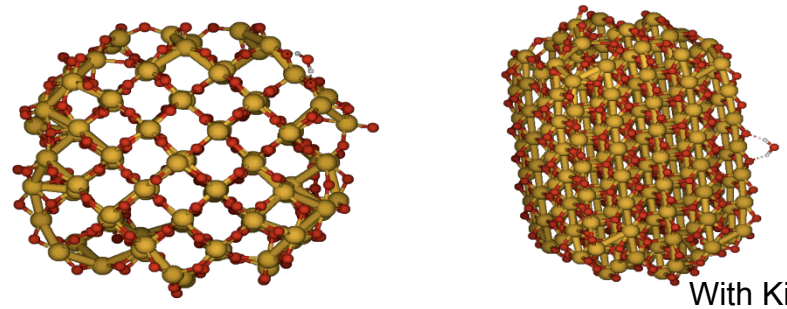


ZnO/H_2O

Partially hydroxyl covered surface

Cu/Zn oxides

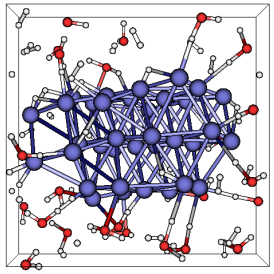
With Raymand & Hermannsson (Uppsala)



With Kim& Kubicki

Water/TiO_2 interactions

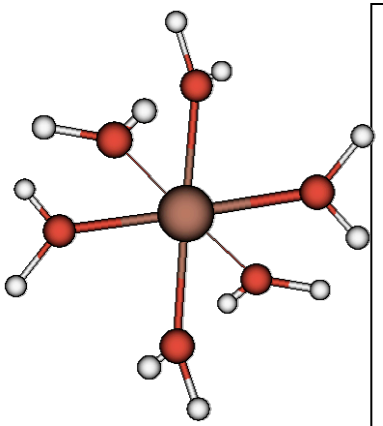
ReaxFF for water



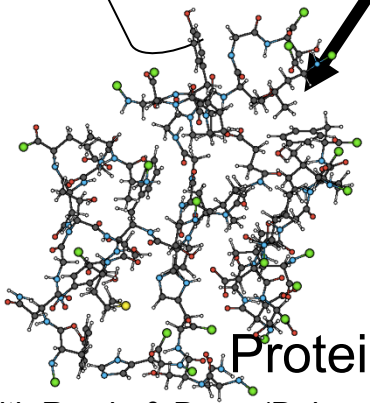
Pt/Ni fuel cells

Nafion fuel cell

Dendrimers/metal cations



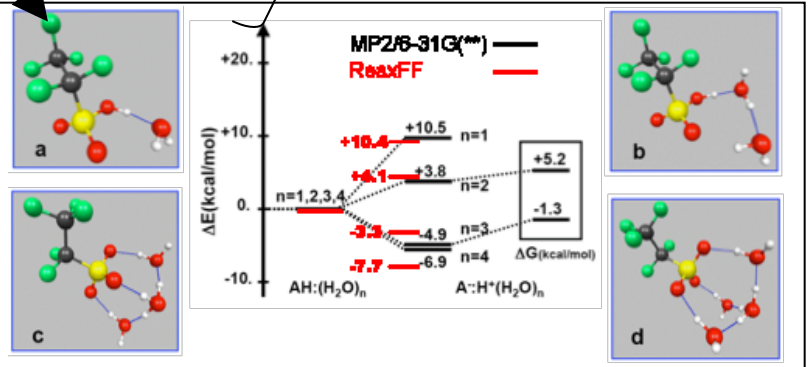
Jahn-Teller distorted $Cu(H_2O)_6^{2+}$-cluster



Proteins

With Ramie & Doren(Delaware)

Enzymes/ DNA/ organic catalysis



Phosphates/sulfonates

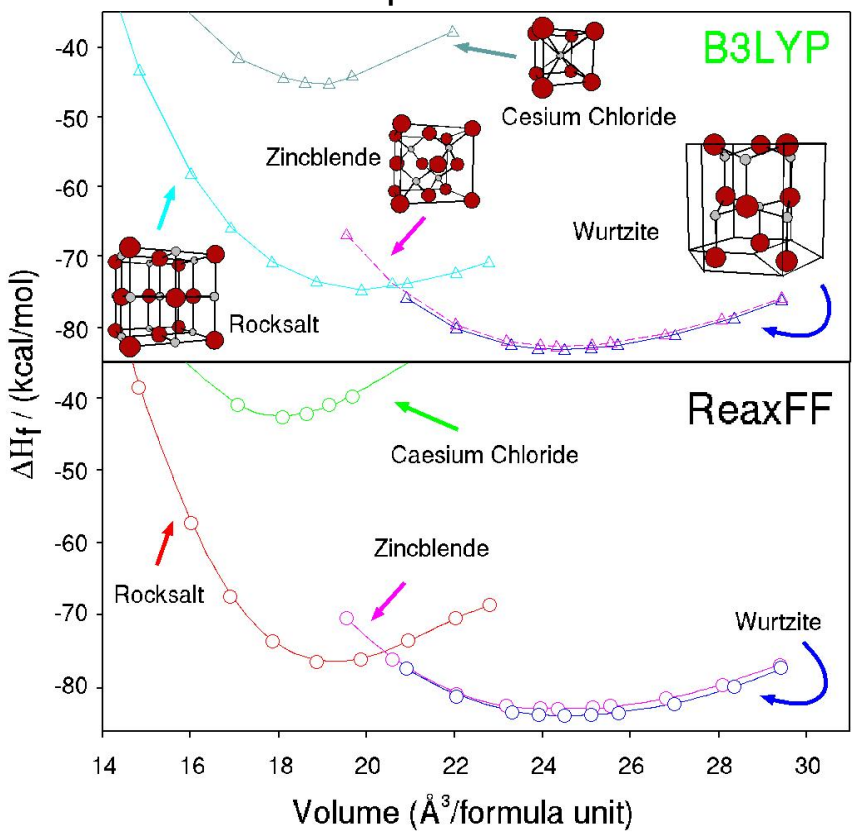
With Ram Devanathan (PNNL))

Simulations of water dissociation on zinc oxide surfaces

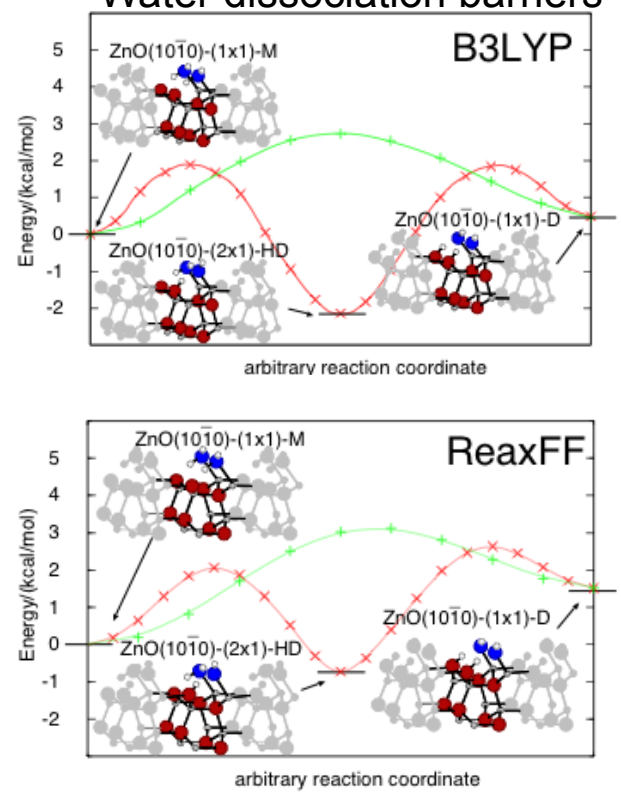
Collaborators: David Raymand and Kersti Hermannson (Uppsala)

B3LYP and ReaxFF equations of state for ZnO-crystal configurations

Bulk equations of state



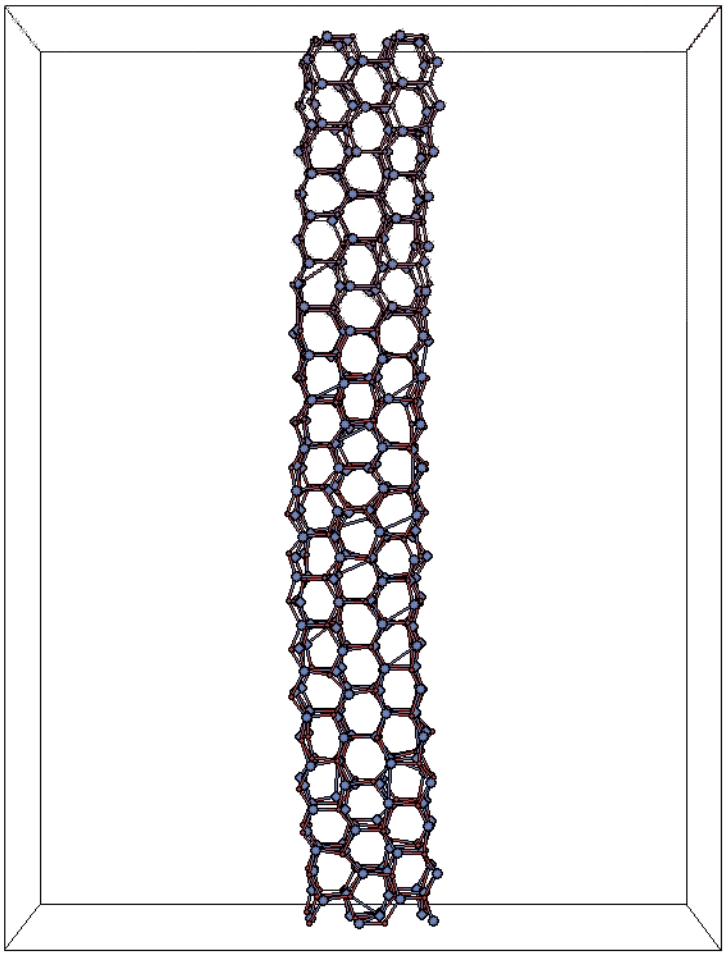
Water dissociation barriers

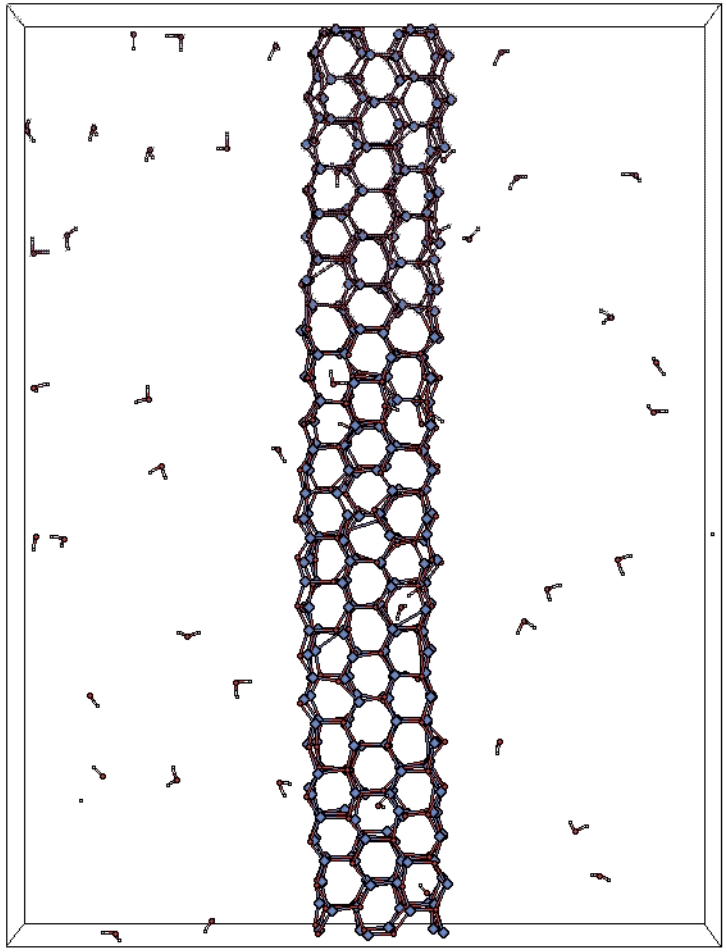


Raymand, van Duin, van Duin, Baudin and Hermannson, Surface Science 2008
Raymand, van Duin, Goddard and Hermannson, Surface Science 2010

Simulation of ZnO nanowire response to local heating

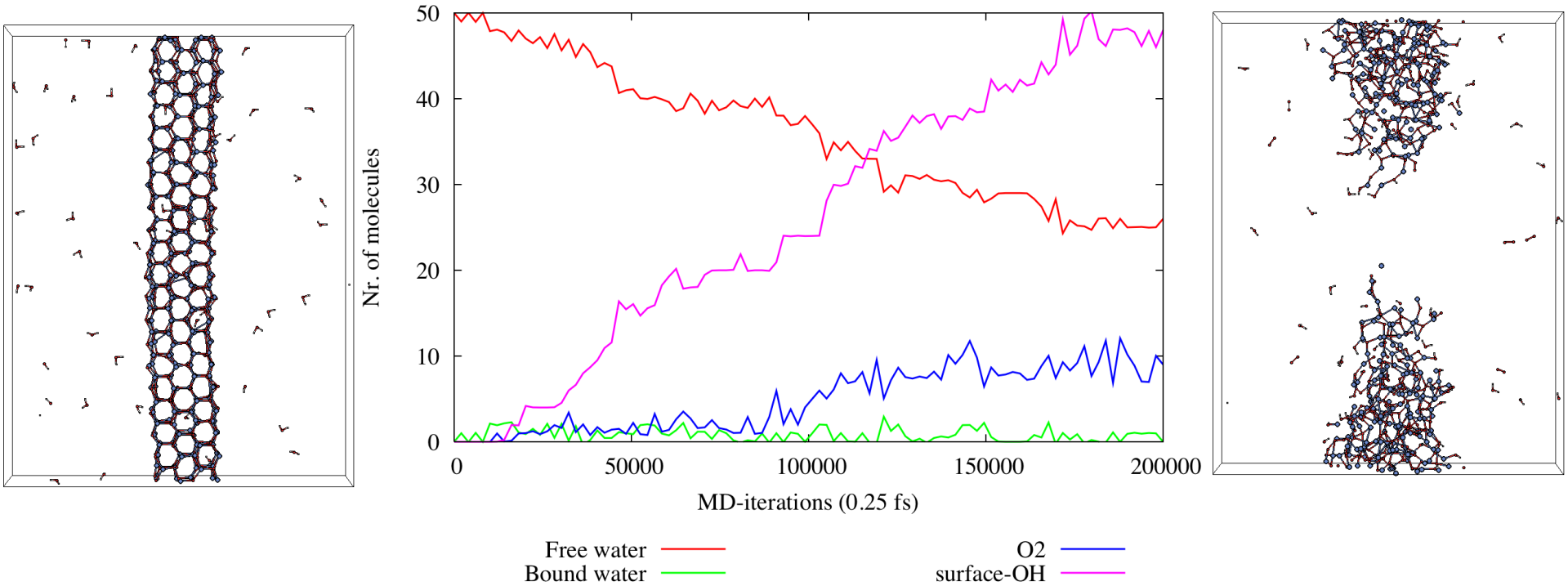
With Mike Russo and Arvind Bharati





Central region: temperature pulse of 2500K
Rest of the structure: NVE-dynamics

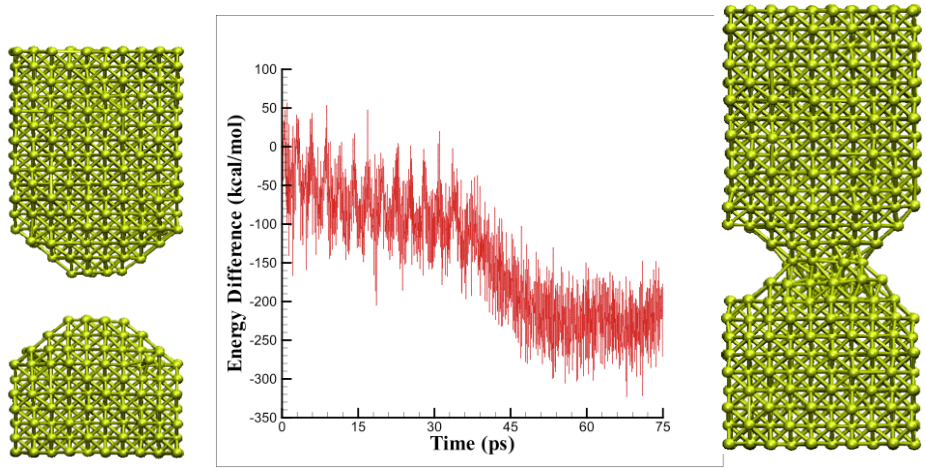
Analysis of ZnO nanowire surface chemistry



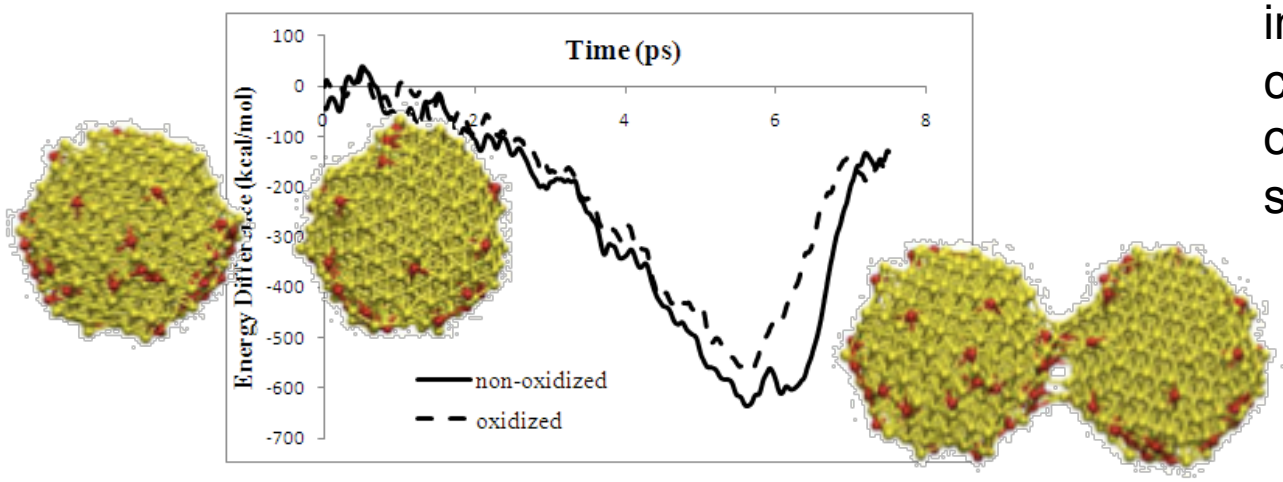
- Rapid adsorption, followed by dissociation, of water molecules
- Dissociated water assists in the breakup of the nanowire
- Release of O_2 molecules from the ZnO-nanowire surface
- ReaxFF can be used to test the high-temperature stability of metal oxide nanowire systems in water vapor
- Extension to Zn/N and Zn/C chemistry (under development) will allow simulations in a combustion environment

Application to cold welding of gold surfaces

With Kaushik Joshi



Simulation of the energy release during interface formation



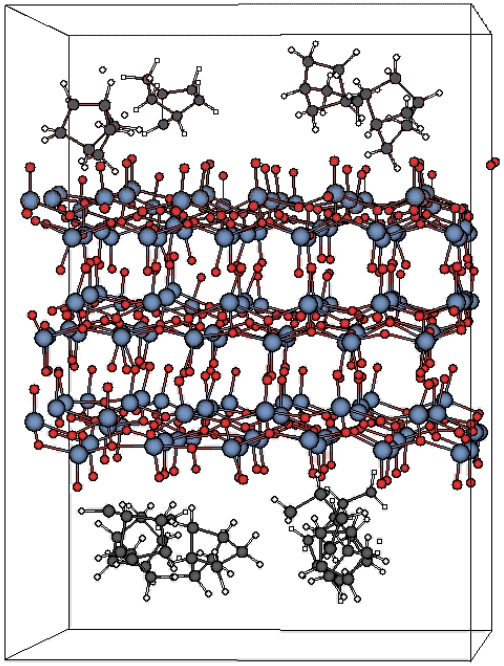
Influence of oxidation on surface cohesion

Joshi, van Duin and Jacob, J.Mat. Chem., in print
Keith, Fantauzzi, Jacob and van Duin, PRB 2010

- Force field simulations allow us to determine energy release, and associated temperature increase, with weld formation.
- We can establish the influence of surface chemistry, in this case oxidation, on weld strength.

Outline

- Simulations on the dynamics of chemical reactions
- The ReaxFF reactive force field
- Overview of ReaxFF applications
    - Combustion reactions
    - Material failure
    - **Catalysis**
- Summary

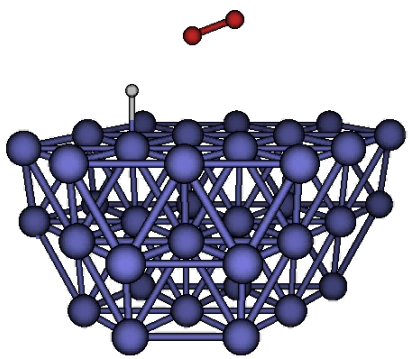


ReaxFF simulation of norbornane decomposition on a V_2O_5 catalyst

Chenoweth et al., JPC-A 2008
Chenoweth et al., Angewandte Chemie 2009

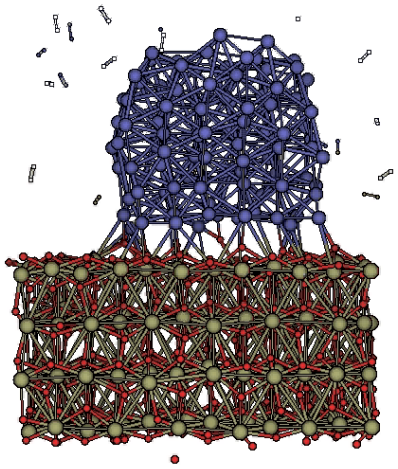
Catalysis

QM



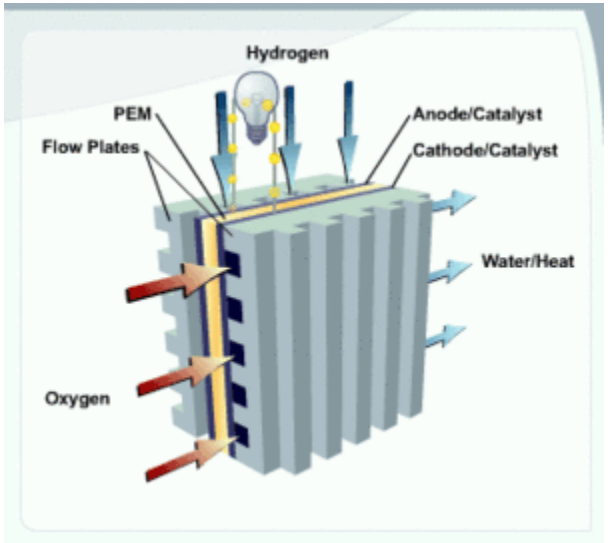
- Accurate energies for key reaction paths
- Size range: up to around 100 atoms

ReaxFF



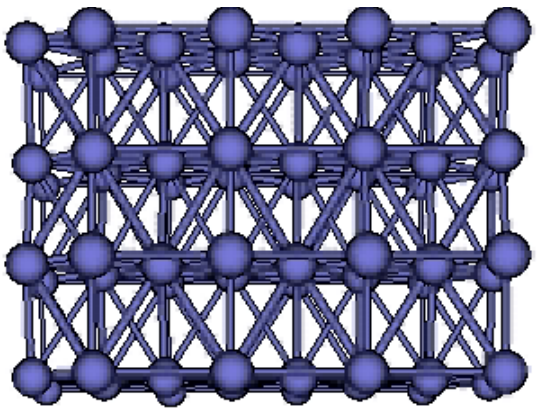
- Allows nanosecond-dynamics on multi-component systems
- Can be parameterized directly from QM

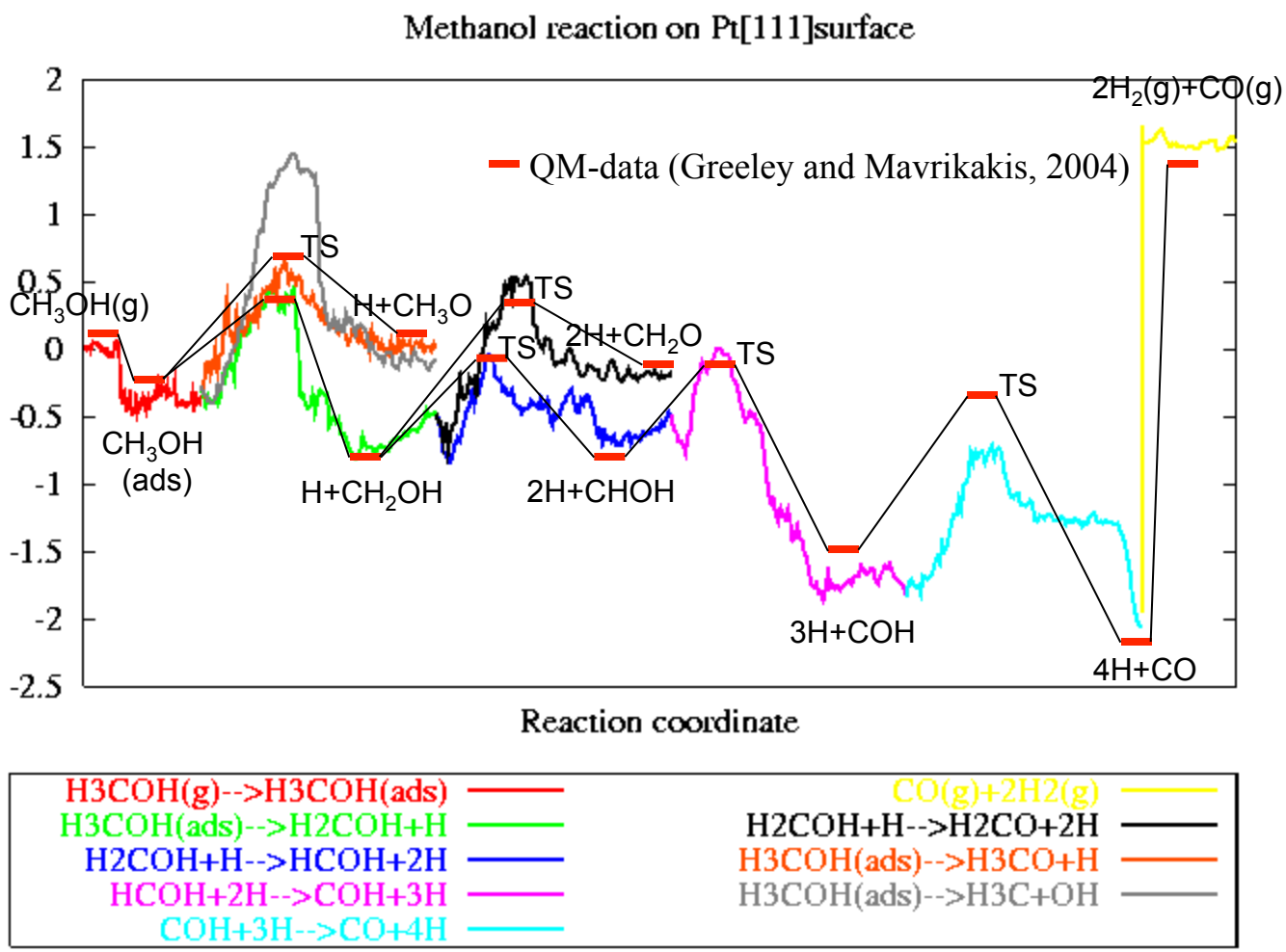
Engineering

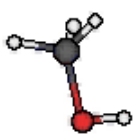


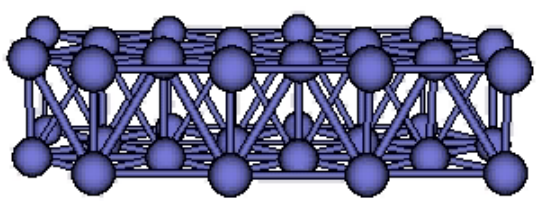
- Interface properties
- Reaction kinetics
- Diffusion constants

QM/ReaxFF methanol reaction pathways





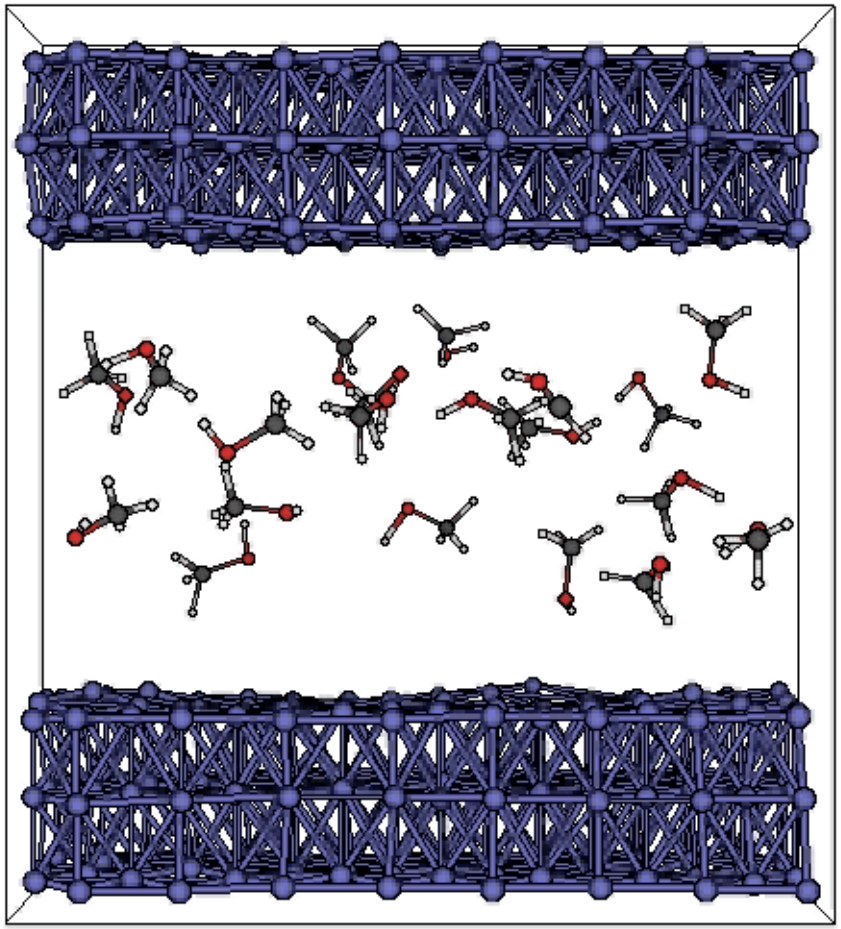


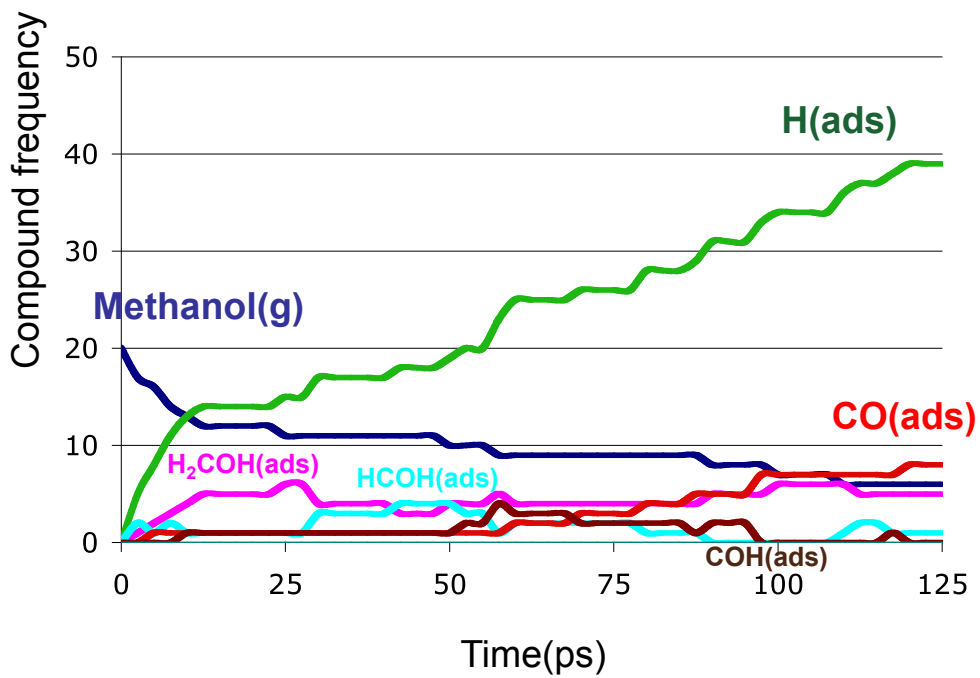


- Excellent agreement between ReaxFF and QM for entire reaction path

Methanol conversion on Pt[111]-surface

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

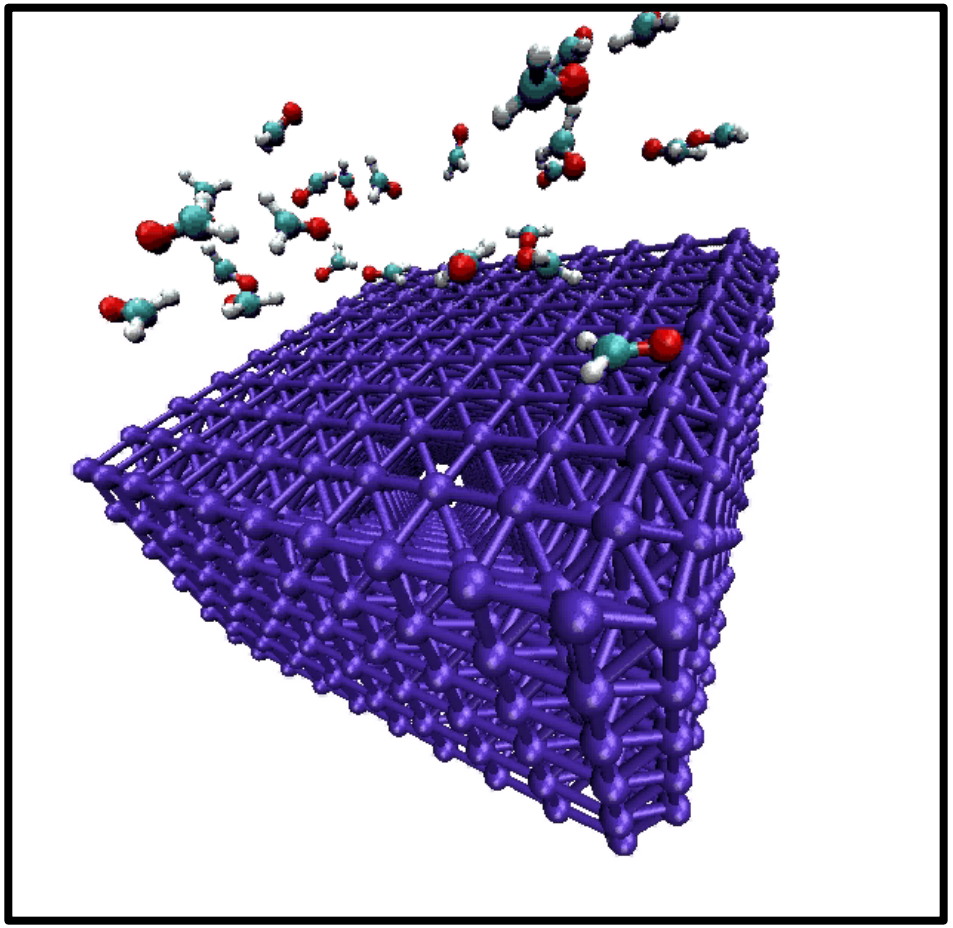


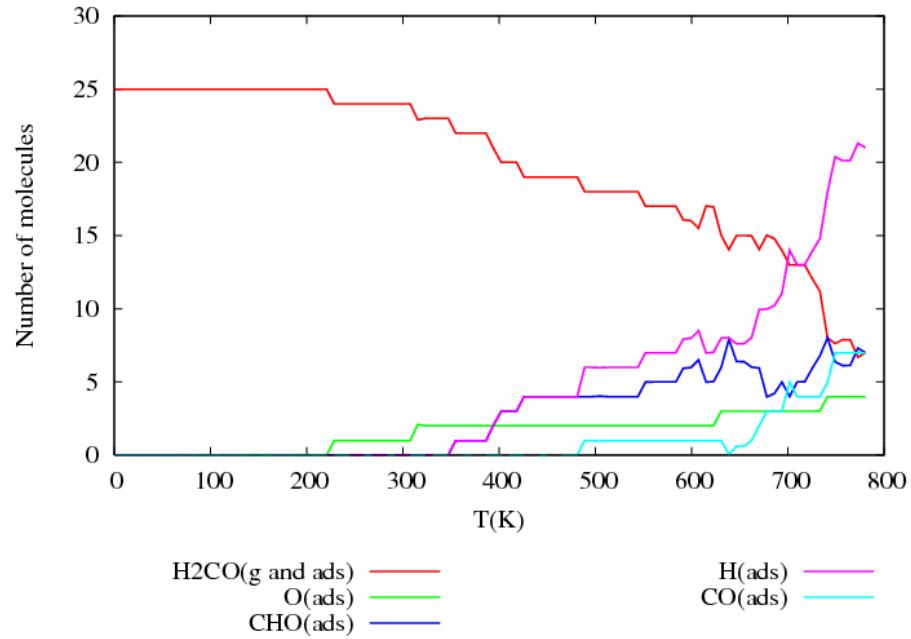


- Methanol dissociates on Pt-surface, generating adsorbed hydrogen
- CO accumulates on surface (poisoning)
- ReaxFF descriptions for Ti, Mo, V, Bi, Ru, Ni available

Metal surface catalysis: Formaldehyde on Fe-cluster

With Takahiro Yamada (U.Dayton); preliminary results



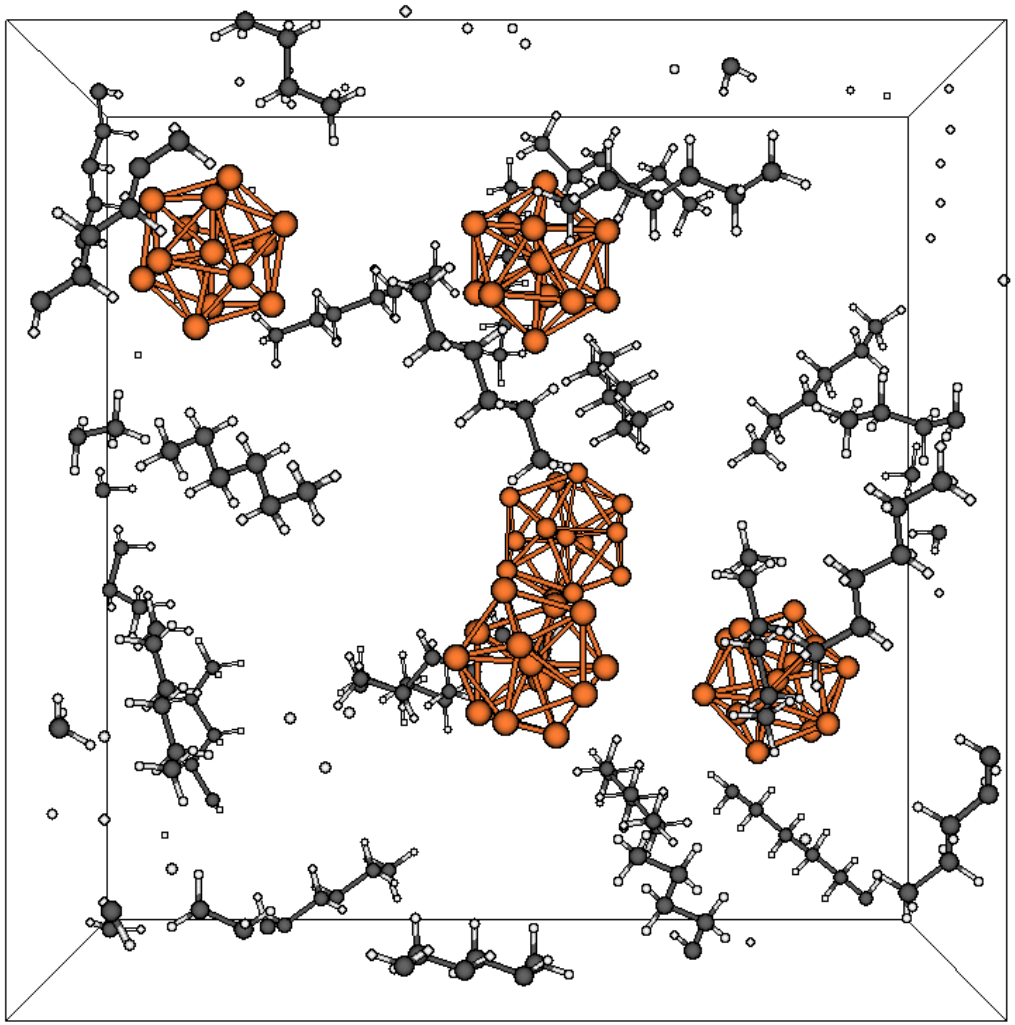


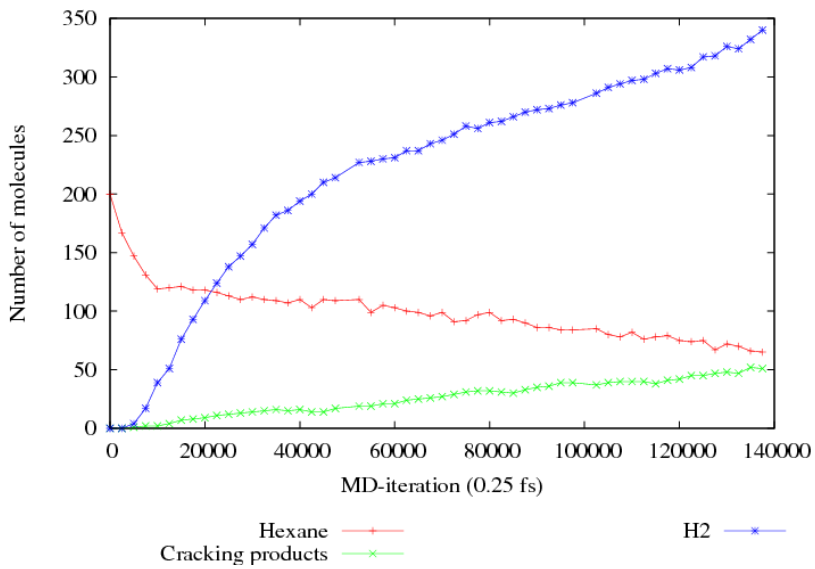
- ReaxFF enables simulation on interface chemistry, including material failure and catalysis

Fe/O ReaxFF: Aryanpour, van Duin and Kubicki, J.Phys.Chem.A 2010

Metal particle catalysis: Hexane cracking on Fe-clusters

With Kaushik Joshi; preliminary results



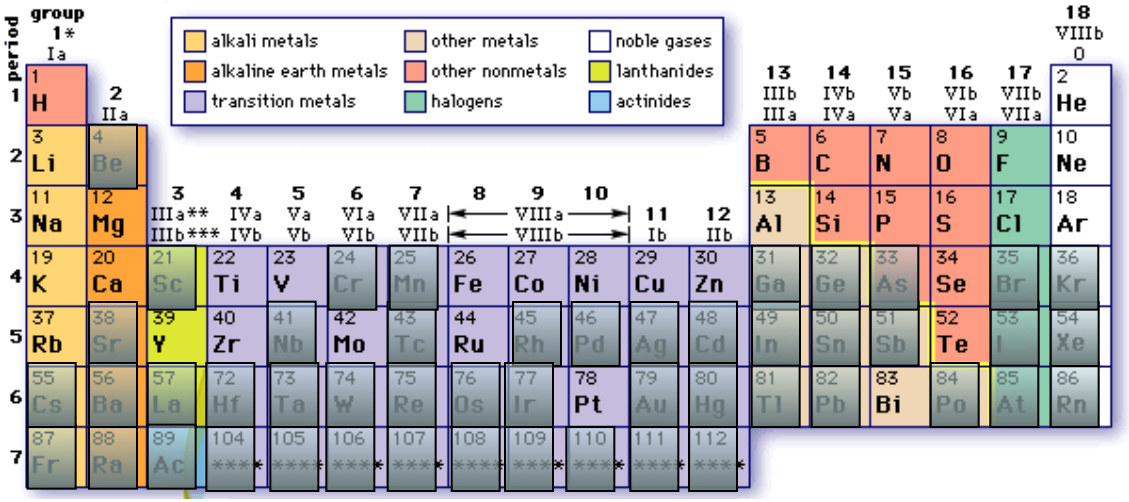


Hexane with Fe_{13} particles, T=1750K

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.



: not currently described by ReaxFF

Acknowledgments

Collaborators:
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- Kimberley Chenoweth, Vyacheslav Bryantsev and Bill Goddard (Caltech)
- Obaidur Rahaman (Ramie) and Doug Doren (U. Delaware)

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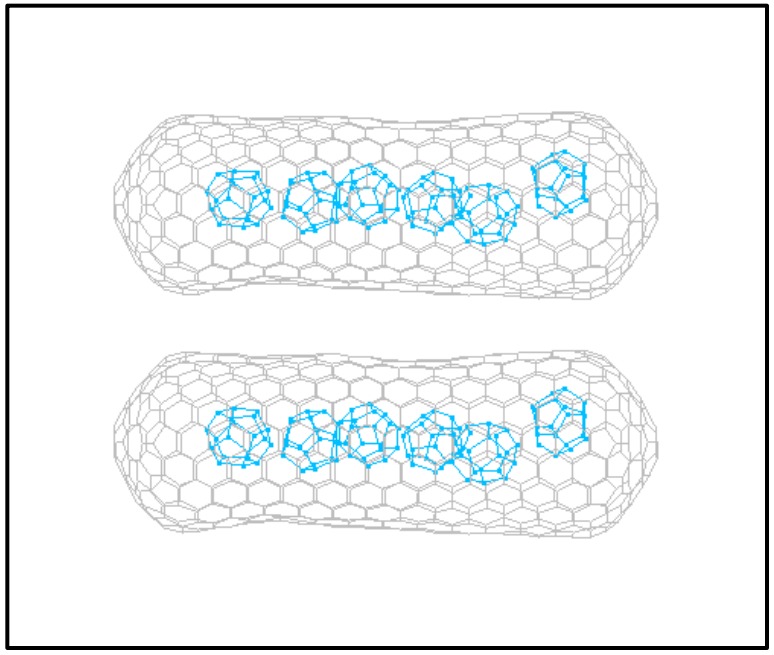
- NSF (TiO_2/water)
- GM and Exxon (ADF integration)
- British Royal Society (initial ReaxFF funding)



ReaxFF simulation of the collision between two closed carbon nanotubes filled with highly-reactive N_{20}-molecules. Impact velocity: 4 km/sec

More information:

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