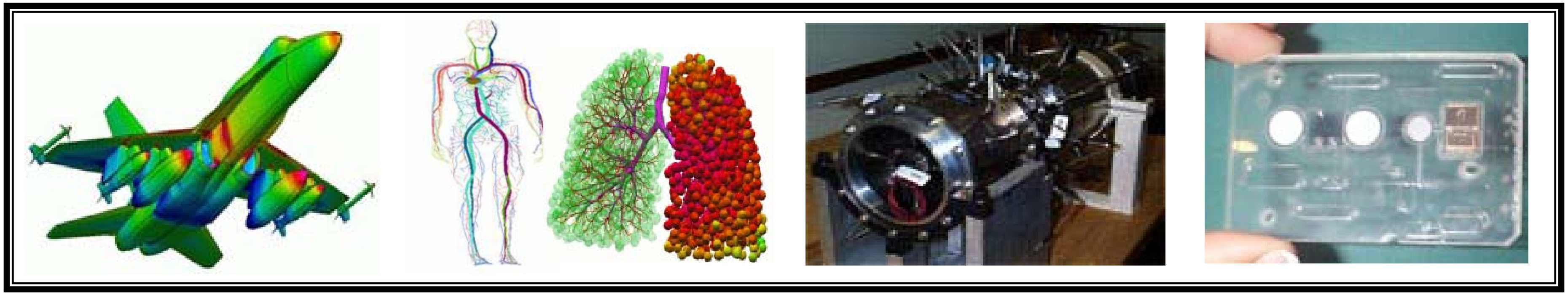
Delivering Breakthrough Solutions

DE-FE0005867 "Computational capabilities for predictions of interactions at the grain boundary of refractory alloys"



Kickoff review presentation

Principal Investigators:

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February, 2011

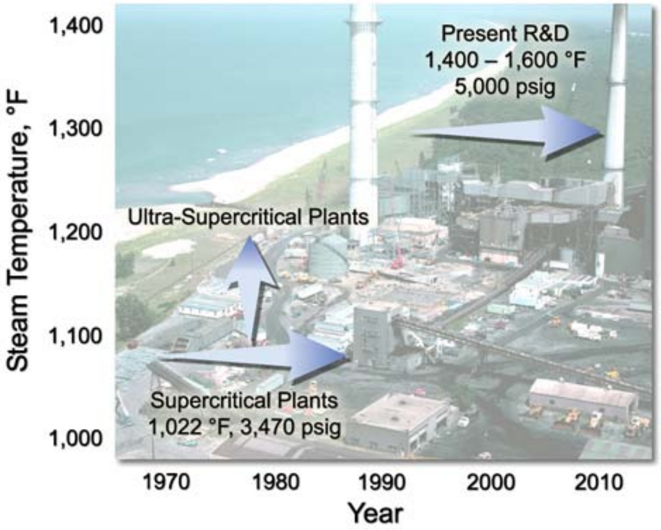
[1] E-mail: avv@cfdrc.com, Phone: 256-726-4886

AGENDA

- Technical background
- Potential breakthrough
- Objectives
- Team
- Technical approach
- Budget and schedule
- Management plan
- Risks and risk management plan
- Status
- Questions and discussion

COMPUTATIONAL DESIGN OF REFRACTORY ALLOYS FOR ENERGY APPLICATIONS

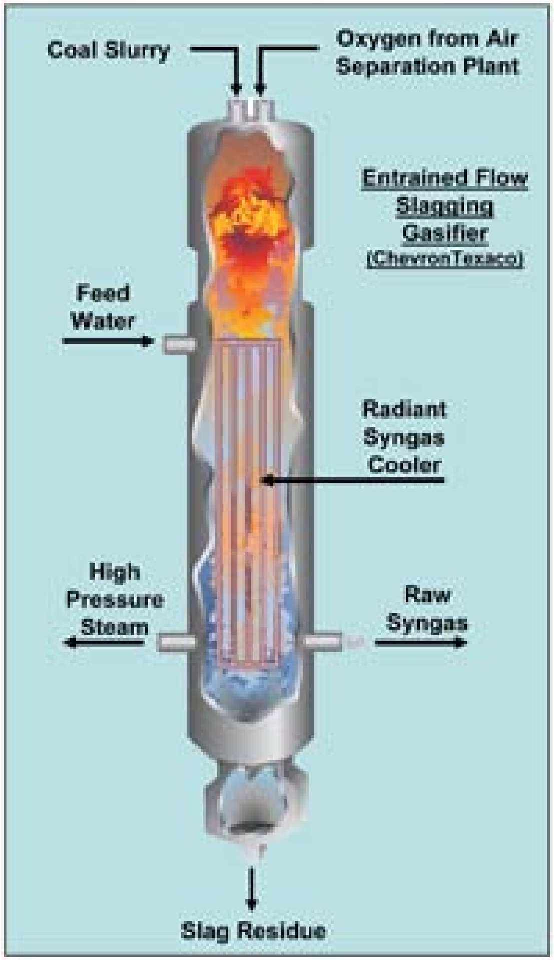
- As stated in the Funding Opportunity Announcement, new high performance refractory alloys are critically required for improving efficiency and decreasing CO_2 emissions of fossil energy systems.
- The development of these materials remains slow because it is driven by a trial-and-error experimental approach and lacks a rational design approach.
- CFD Research Corporation (CFDRC) and Pennsylvania State University (PSU) have teamed in this project to develop, demonstrate, and validate computational capabilities for predictive analysis of interactions at the grain boundary of refractory alloys.



Increase in Steam Temperature and Pressure in Coal-Fired Power Plants

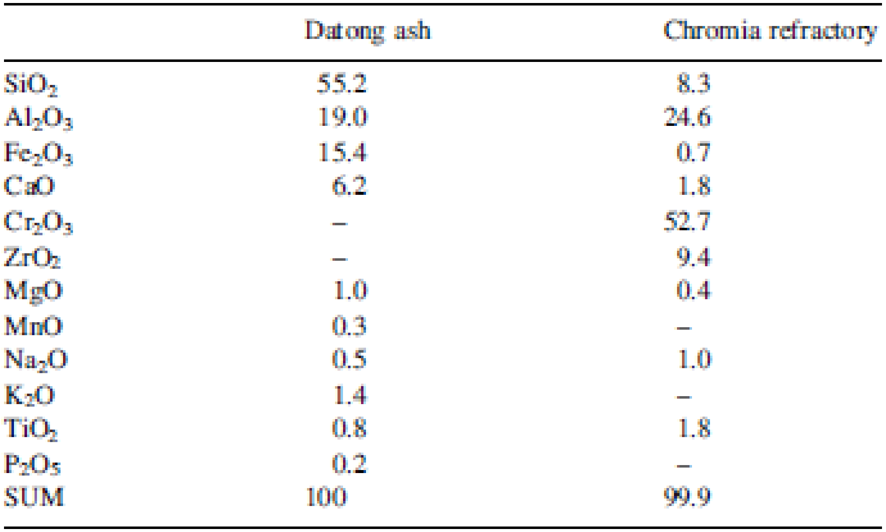
COMPUTATIONAL DESIGN OF REFRACTORY ALLOYS FOR ENERGY APPLICATIONS (CONT.)

- High-chromia refractories could last ~ 3.5 years in a slagging coal gasifier under optimum conditions (Fahrion et al 1999).
- However, commercial gasifiers must often use suboptimal feed stocks and operating conditions, and the refractory lifetime is often reduced to < 1.5 years (Stiegel et al 2006).
- The expense of refractory replacement in a large-scale gasifier can exceed $1 M (Stiegel et al 2006).
- One of the most frequently cited R&D needs is improvement of fundamental understanding of refractory alloy degradation mechanism.



REFRACTORY ALLOYS AND SLAG COMPOSITION

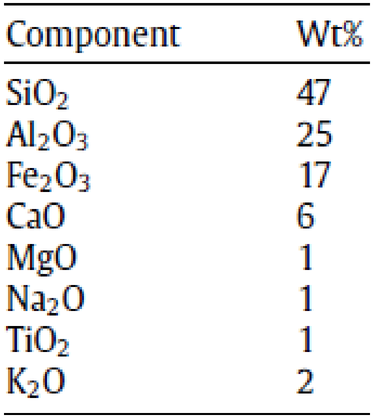
- Majority of reported refractory alloys utilized in a slagging coal gasifier are chromia (Cr_2O_3) and alumina (Al_2O_3) based refractories.
- Chrome oxide materials showed low chemical solubility in gasifier slags by forming high melting spinels/solid solutions with iron oxides (Bennett 2007 and Kim et al 2008).
- In the past, non-chromia refractory compositions did not show comparable performance to high chrome oxide refractory materials.
- Only a few materials (ZrO_2 etc.) have the potential to resist slag corrosion as well as chrome oxide.



	Datong ash	Chromia refractory
SiO_2	55.2	8.3
Al_2O_3	19.0	24.6
Fe_2O_3	15.4	0.7
CaO	6.2	1.8
Cr_2O_3	–	52.7
ZrO_2	–	9.4
MgO	1.0	0.4
MnO	0.3	–
Na_2O	0.5	1.0
K_2O	1.4	–
TiO_2	0.8	1.8
P_2O_5	0.2	–
SUM	100	99.9

- Refractories and ash (wt %), Kim et al 2008

Component	Wt %
Cr_2O_3	92
Al_2O_3	4.7
P_2O_5	3.3



Component	Wt%
SiO_2	47
Al_2O_3	25
Fe_2O_3	17
CaO	6
MgO	1
Na_2O	1
TiO_2	1
K_2O	2

- Refractories and ash, Besmann 2008

FAILURE MECHANISMS OF SLAGGING COAL GASIFIER

- **Slagging coal gasifier typically operates at high temperature (1300–1600 C) and pressure (2–3 MPa) conditions (Williford et al 2008).**
- **Industrial refractories have a finite amount of porosity, including initial flaws and joints between bricks.**
- **These defects are responsible for penetration of the slag into the interior of the refractory by permeation and infiltration mechanisms assisted by the pressure gradients within the gasifier, along with capillary and diffusive intrusion mechanisms.**
- **The thermal– chemical–mechanical interactions between the refractory and slag result in degradation by corrosion, erosion, cracking, and spalling.**

SLAG/REFRACTORY INTERFACE REACTIONS

- Slag penetration and chemical corrosion are the primary causes for refractory degradation in a gasifier (Bennett, et al., 2007 and Kim et al. 2008).
- Dominant reaction product at the slag/refractory interface $(Fe,Cr)_3O_4$ is formed as a result of the following reaction:

$$Fe_2O_3\ (slag) + Cr_2O_3\ (refractory) \rightarrow (Fe,Cr)_3O_4 \qquad (R1)$$

- Once Fe in the slag is depleted, Al_2O_3 in the slag interacted with Cr_2O_3:

$$Al_2O_3\ (slag) + Cr_2O_3\ (refractory) \rightarrow (Cr,Al)_2O_3 \qquad (R2)$$

- It was found that the densified large Cr_2O_3 grains were less affected by the reaction (R2) than the Cr_2O_3 small particles observed in the refractory alloys before the tests.

SULFUR SEGREGATION

- In contrast to Al, Fe, or Si, which can oxidize beneath the scale, sulfur (S) can deteriorate the adhesion of the scale.
- Upon oxidation of high temperature alloys such as Fe-Cr-Al and Ni-Cr-Al, the solubility limit of CrS can be exceeded, and such sulfide precipitates initiating the segregation.
- According to thermodynamics it is nearly impossible to replace oxygen – metal bonds by sulfur – metal bonds.
- As soon as a void or a microcrack is formed at the interface, sulfur segregates to the fresh metal surface formed.
- Sulfur surface segregation decreases the metal surface energy, thereby voids and cracks are stabilized and their growth is accelerated.

SULFUR SEGREGATION IN AL2O3-BASED ALLOYS

- Hou et al 2008 concluded that
  - During high-temperature (T > 900°C) oxidation of Al_2O_3-based alloys, S is the only nonmetallic impurity that consistently segregates at the growing interface and weakens the interfacial strength;
  - S is able to segregate to Al_2O_3/Fe/Al interfaces only when a complete layer of α-Al_2O_3 is developed;
  - Small amounts of reactive elements (<0.1 at%) added in Ni- or Fe-based alloys prevent S segregation to the Al_2O_3/alloy interface, and the reactive element that segregate to interfaces further increase the interfacial strength;
  - S and Cr co-segregate to the interface, causing an increase in the interfacial S concentration;
  - Pt eliminates S segregation at alumina/β-Ni/Pt/Al interfaces and reduces it when the alloy is the γ/γ′ phase.
- We will reproduce these trends using proposed ReaxFF potential.

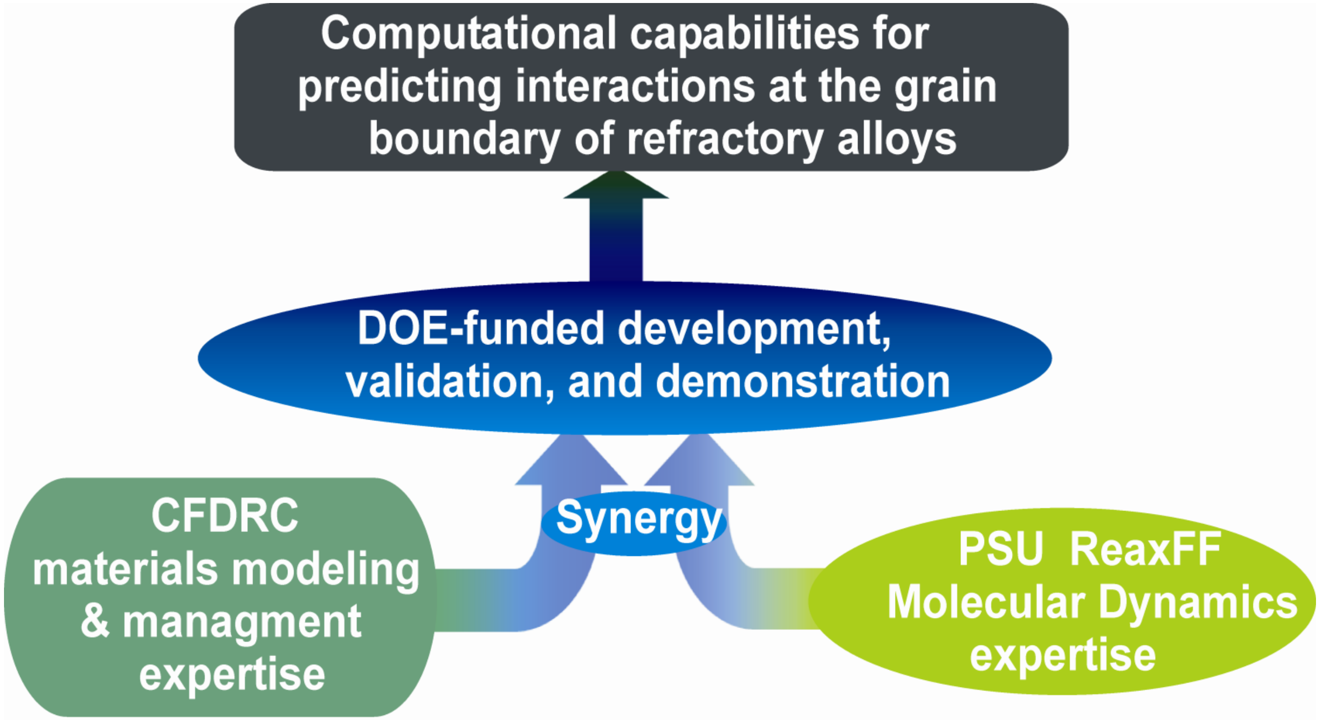
POTENTIAL TO CONTRIBUTE TO A SCIENTIFIC BREAKTHROUGH

- **Atomistic design has the potential to accelerate the development of new materials through the prediction of mechanical properties, corrosion and segregation resistance.**
- **The success of atomistic simulations critically depends on the fidelity of available interatomic potentials.**
- **Existing interatomic potentials of metallic alloys are typically derived and optimized against a small number of validating experiments, and typically are not able to account for reactions, or are not applicable for high-temperature simulations.**
- **These critical deficiencies will be addressed in the proposed work by developing, demonstrating, and validating Quantum Mechanic (QM) based ReaxFF potentials integrated into an open-source MD code, the LAMMPS-MD simulator developed by Sandia National Laboratories.**

POTENTIAL TO CONTRIBUTE TO A SCIENTIFIC BREAKTHROUGH (CONT.)

- ReaxFF potentials capable of naturally accounting for grain boundary types and types of segregants (substitutional and interstitial) will be developed.
- These potentials will offer a compromise between high-level QM description and computational speed.
- Proposed computational capabilities will be demonstrated to provide insight to the mechanism of segregation at the grain boundaries of slagging gasifier refractories
- CFDRC/PSU plan to file patent applications describing approaches to limit sulfur and other impurities segregation at the grain boundaries of refractories.

OVERALL PROJECT OBJECTIVES



Computational capabilities for predicting interactions at the grain boundary of refractory alloys

DOE-funded development, validation, and demonstration

Synergy

CFDRC materials modeling & managment expertise

PSU ReaxFF Molecular Dynamics expertise

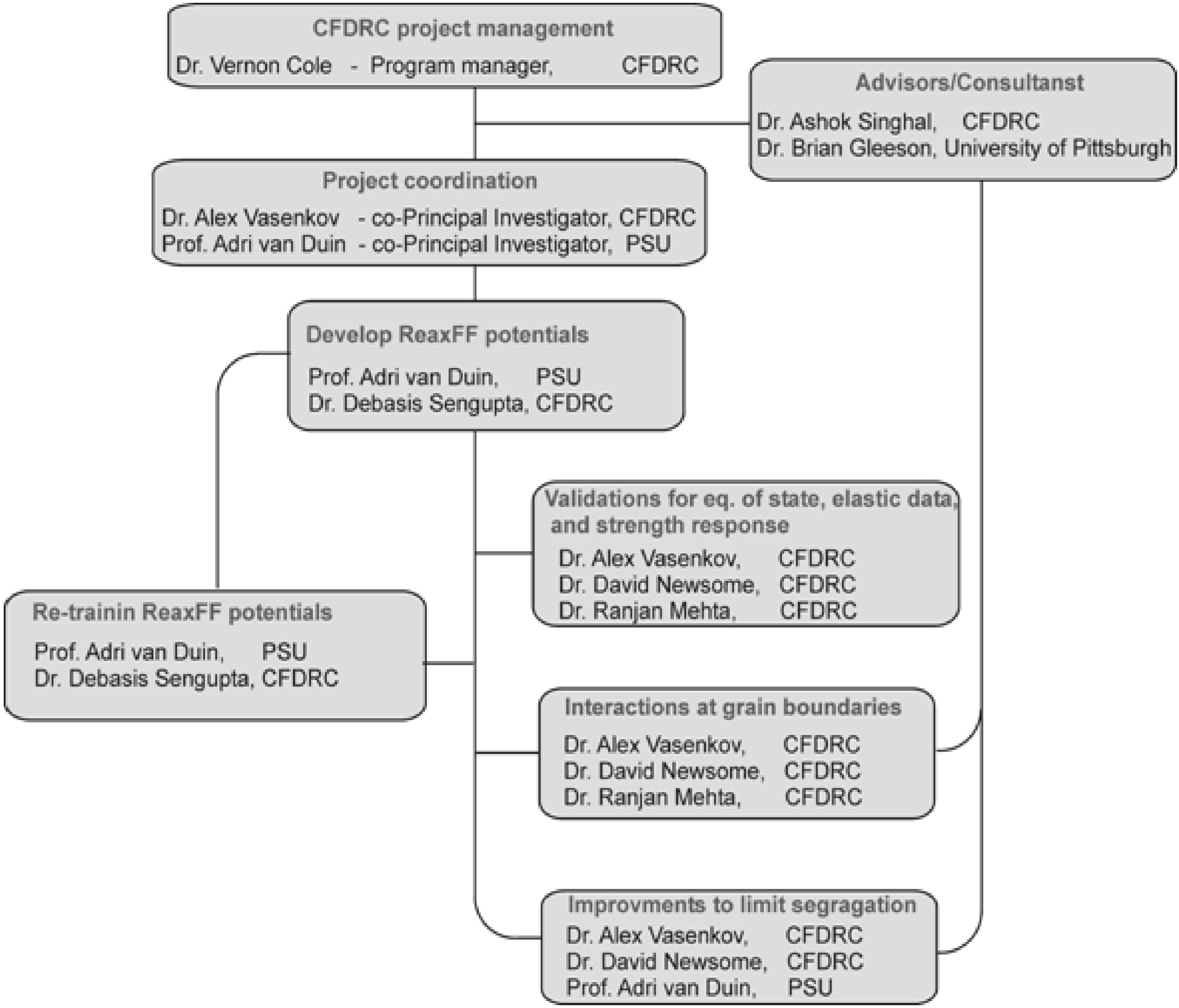
- The overall objectives of the proposed project are:
  - ➢ Develop computational capabilities for predictive analysis of grain boundary interactions using large-scale ReaxFF-MD simulations
  - ➢ Assess degradation mechanisms, and
  - ➢ Design approach to limit segregation at the grain boundaries of refractories for coal gasification and related processes.

SPECIFIC PROJECT OBJECTIVES

- More specific technical objectives are as follows:
  - Demonstrate the feasibility by reproducing trends observed for elemental segregation and reactions at the grain boundaries of Al_2O_3 based refractories;
  - Develop ReaxFF potentials for predictive MD modeling of interactions with impurities at the grain boundary of Cr_2O_3 based refractories;
  - Validate ReaxFF potentials against literature data for equation of state and elastic data;
  - Demonstrate the feasibility to reproduce major reaction pathways during interaction of slag with refractories in a typical slagging gasifier environment;
  - Determine mechanisms of segregation at the grain boundary of Cr_2O_3/Al_2O_3 based refractories and validate the predictions against the literature results;
  - Identify approaches to limit sulfur segregation at the grain boundaries of $Cr_2O_3/Al_2O_3/P_2O_5$ refractory.

TEAM

- **CFDRC has over 20 years of experience developing and commercializing new technologies.**
- **Most recent example is an ongoing $5M grant from the DOE Hydrogen Fuel Cell Program, managed by Dr. Cole, the director of the proposed work.**
- **The proposed work will be complemented by the current DOE SBIR project whose goal is to develop database of ReaxFF reactive potentials for Mo, Mo-Ni, Mo-O, and Mo-H_2S.**



CFDRC project management
Dr. Vernon Cole - Program manager, CFDRC

Advisors/Consultanst
Dr. Ashok Singhal, CFDRC
Dr. Brian Gleeson, University of Pittsburgh

Project coordination
Dr. Alex Vasenkov - co-Principal Investigator, CFDRC
Prof. Adri van Duin - co-Principal Investigator, PSU

Develop ReaxFF potentials
Prof. Adri van Duin, PSU
Dr. Debasis Sengupta, CFDRC

Validations for eq. of state, elastic data, and strength response
Dr. Alex Vasenkov, CFDRC
Dr. David Newsome, CFDRC
Dr. Ranjan Mehta, CFDRC

Re-trainin ReaxFF potentials
Prof. Adri van Duin, PSU
Dr. Debasis Sengupta, CFDRC

Interactions at grain boundaries
Dr. Alex Vasenkov, CFDRC
Dr. David Newsome, CFDRC
Dr. Ranjan Mehta, CFDRC

Improvments to limit segragation
Dr. Alex Vasenkov, CFDRC
Dr. David Newsome, CFDRC
Prof. Adri van Duin, PSU

CFD Research Corporation

Advanced Technology and Service Company

- Supporting Federal Agencies and global businesses since1987
- Over 70% staff with advanced degrees
- 45+ patents (awarded & pending)

CFDRC develops cutting-edge technologies and provides innovative solutions for:

Energy & Materials

Biomedical & Life Sciences

Aerospace & Defense

HQ – Huntsville, AL

Bio-Laboratories
HAIB, Huntsville, AL

Engineering T&E
Scottsboro, AL

Gov't Sites

MSFC, Huntsville, AL
USAARL,Ft. Rucker, AL

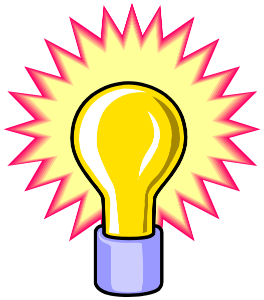
Why CFDRC? *Valuable Technology Partner*

Pioneering Physics-based Simulations

Coupled Multi-physics, Multi-scale, Multi-fidelity simulations of fluid, thermal, chemical, mechanical, electrical and biological phenomena for **real world** applications.

→ ***Better insights and better decisions for:***

- new concepts and designs
- improved operations and safety
- reduced development time and cost



Complimentary Design, Fabrication, T&E Expertise and Facilities for:

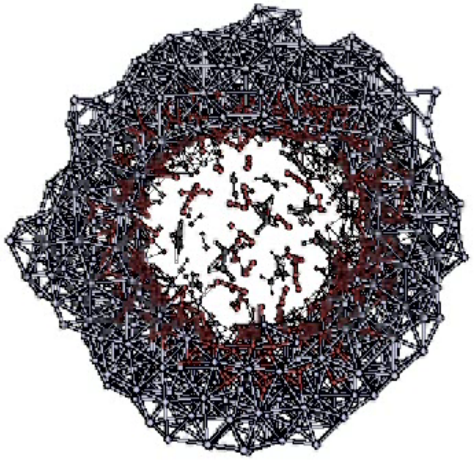
- Combustion, Propulsion and power systems
- Biomedical and Energy devices

→ ***Facilitates better products & better systems.***

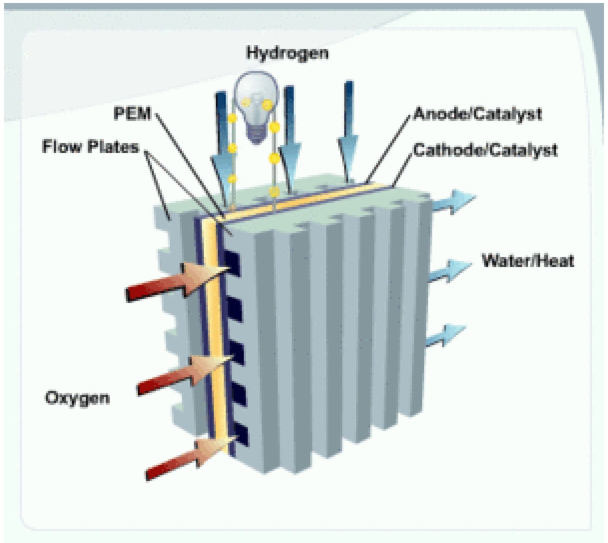
Engineering Challenges….

Coal power plant

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

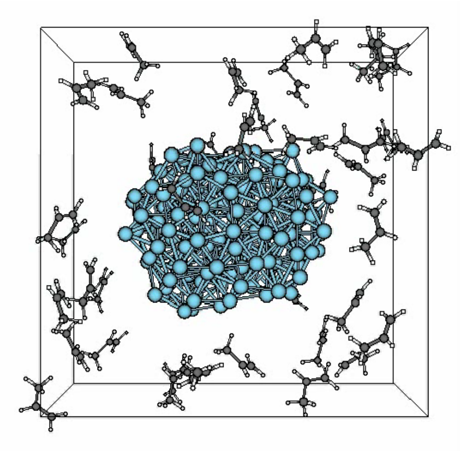


Pre-oxidized Al-tube with ethylene/O_2/ozone mixture



Fuel cell

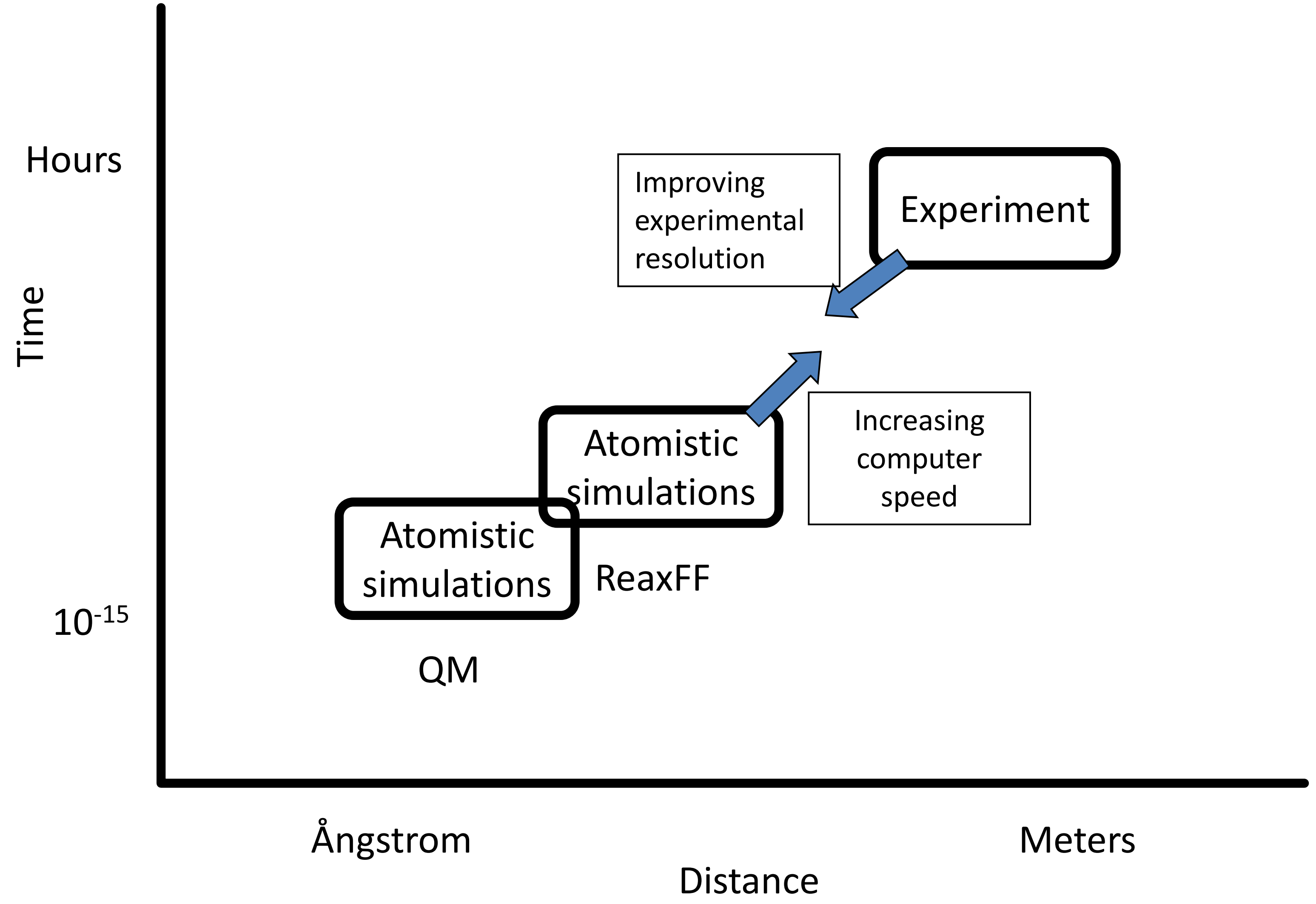
- Higher efficiency
- Longer lifetime
- Cheaper
- Need new, cheap catalyst materials that are resistant to poisoning



Ni-particle reacting with propene at T=1500K

…require atomistic-scale solutions

Solving the Size/Time Gap Between Simulation and Experiment



Hours

Time

10^{-15}

Improving experimental resolution

Experiment

Atomistic simulations

Increasing computer speed

Atomistic simulations

ReaxFF

QM

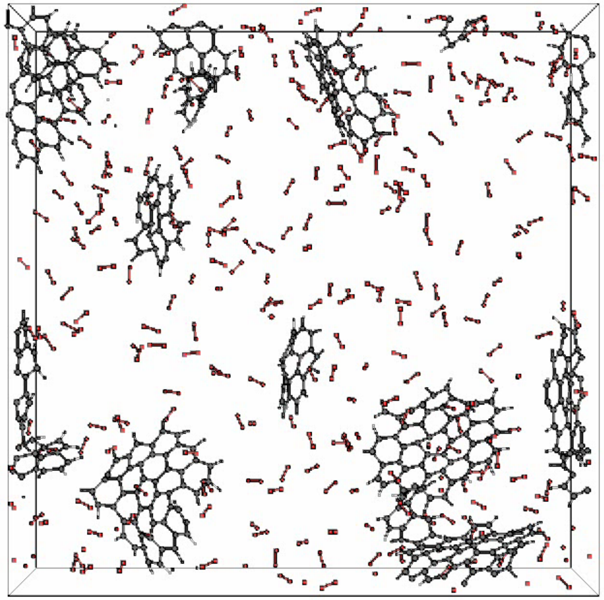
Ångstrom

Meters

Distance

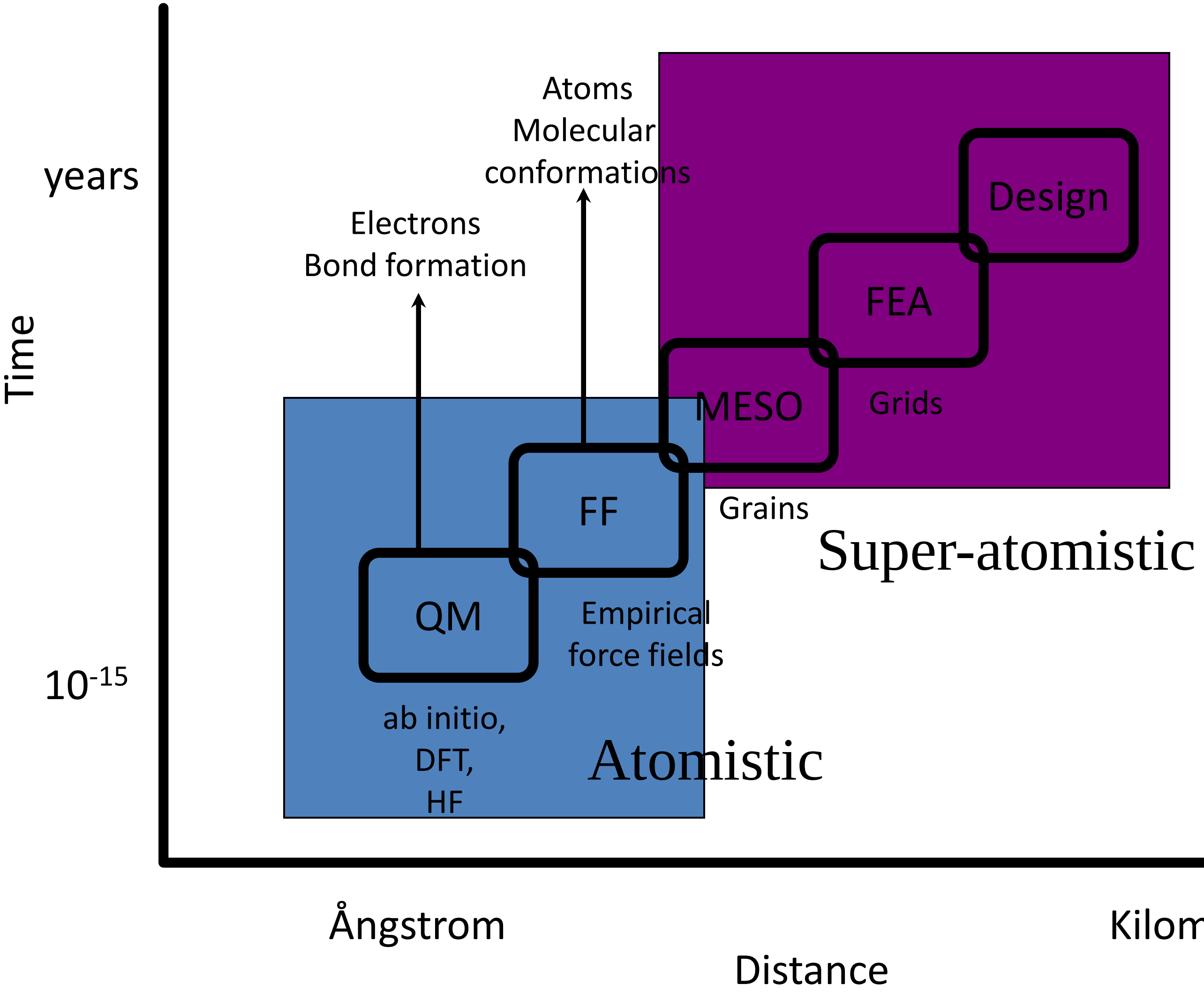
Outline

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



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

Simulations on the Dynamics of Chemical Reactions

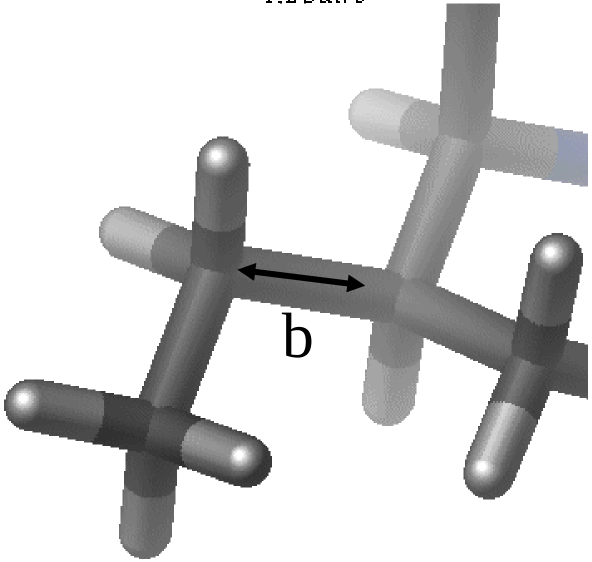


QM methods:
- Fundamental
- Expensive, only small systems

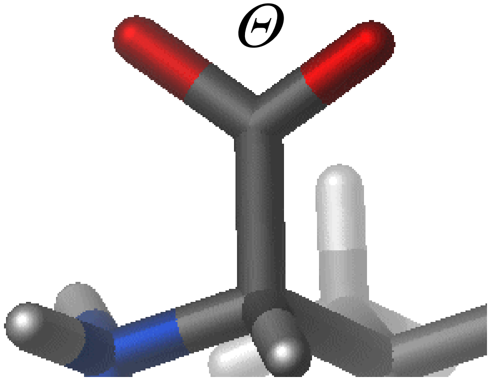
FF methods
- Empirical; need to be trained
- Much cheaper than QM, can be applied to much larger systems

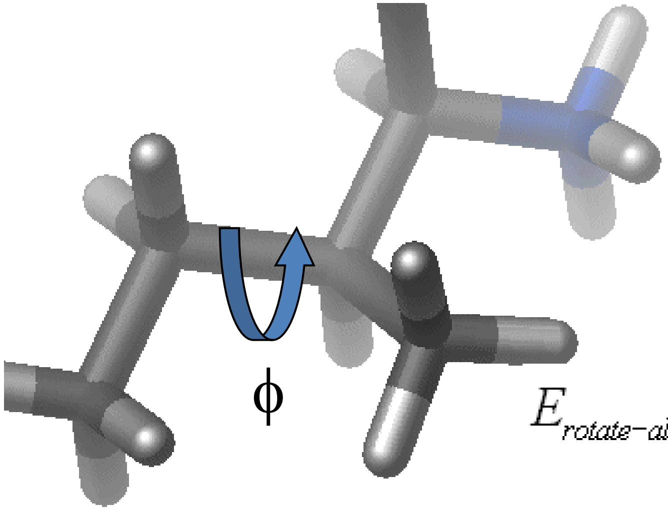
Force Field Methods

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



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





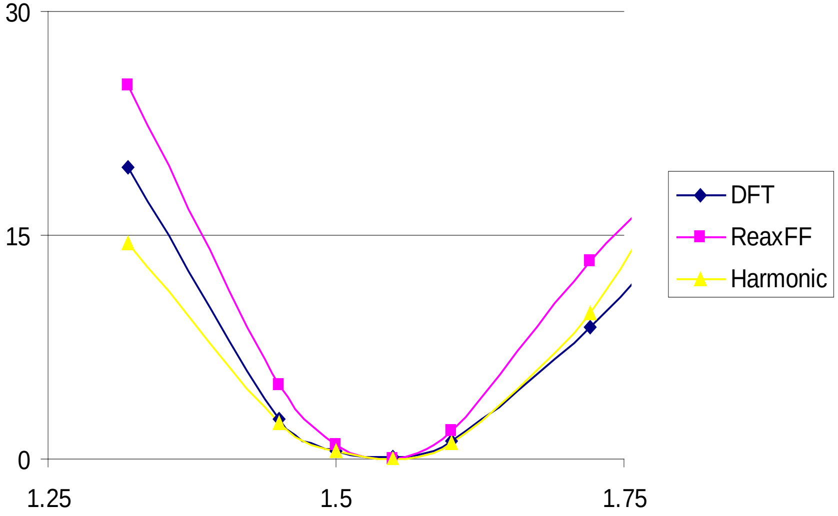
$$E_{rotate-along-bond} = \sum_{1,4\,pairs} K_\phi \left(1 - \cos\left(n\phi\right)\right)$$

- 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

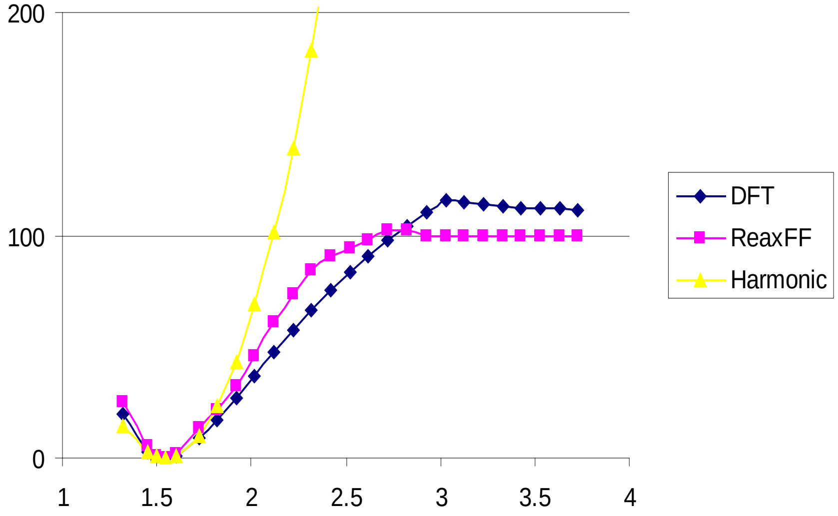
Failure of the Harmonic Model

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

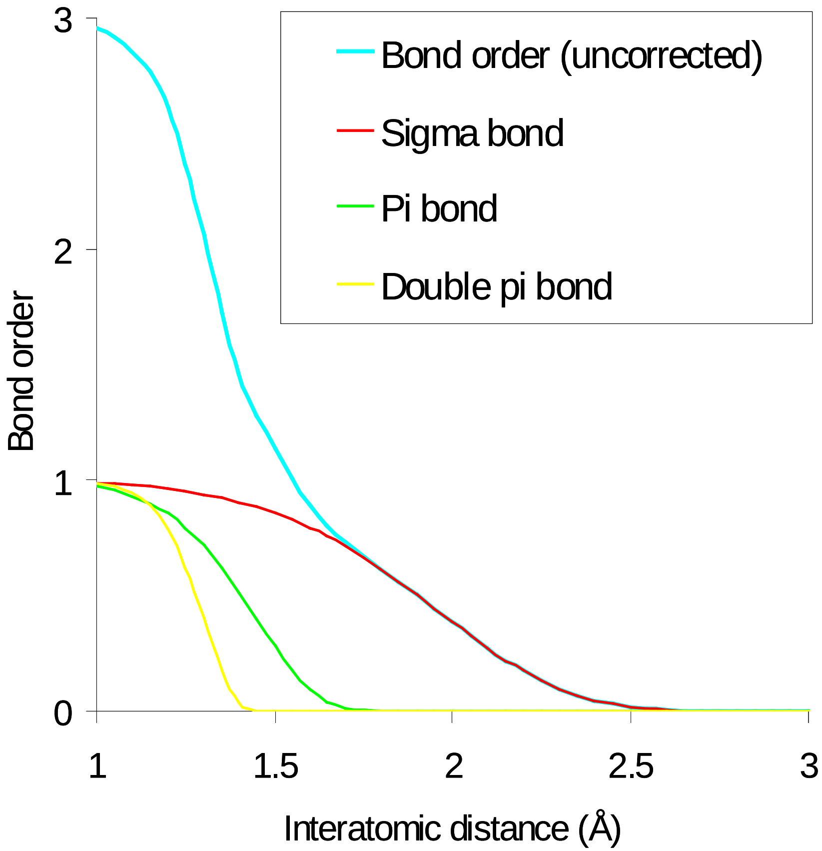
- To get a smooth transition from nonbonded to single, double and triple bonded systems ReaxFF employs a bond length/bond order relationship [1-3]. Bond orders are updated every iteration.
- All connectivity-dependent interactions (i.e. valence and torsion angles, H-bond) are made bond-order dependent, 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.

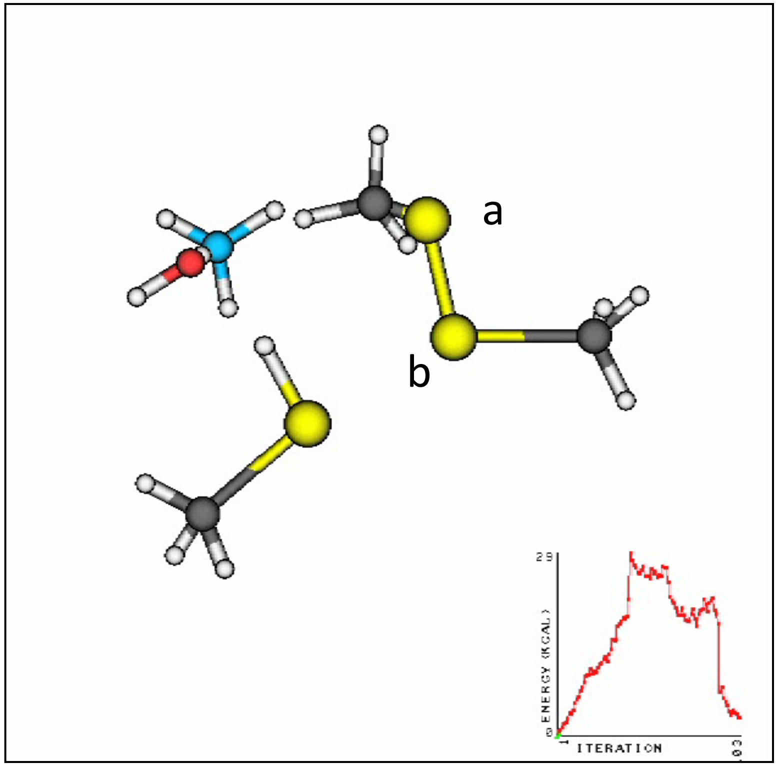
Bond Orders

Calculation of bond orders from interatomic distances

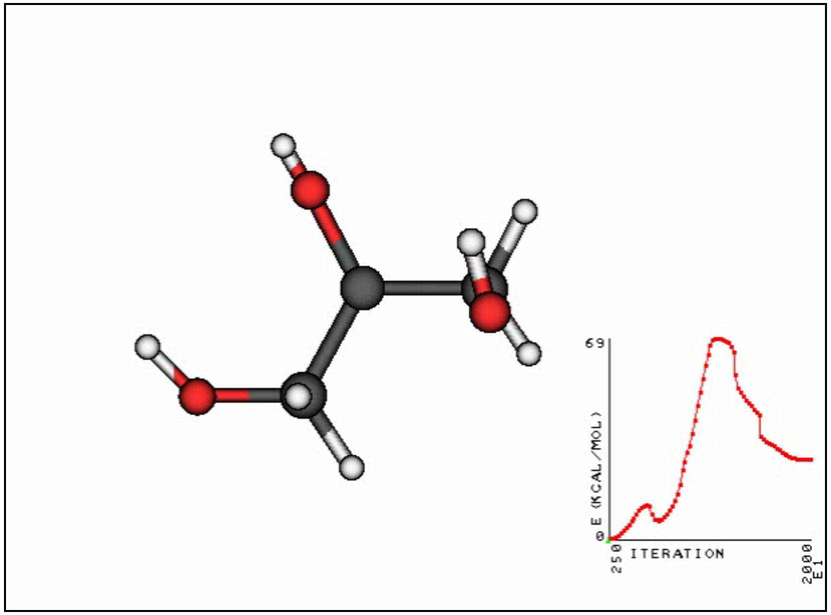
$$BO_{ij}^{'} = \exp\left[p_{bo,1} \cdot \left(\frac{r_{ij}}{r_o^{\sigma}} \right)^{p_{bo,2}} \right] + \exp\left[p_{bo,3} \cdot \left(\frac{r_{ij}}{r_o^{\pi}} \right)^{p_{bo,4}} \right] + \exp\left[p_{bo,5} \cdot \left(\frac{r_{ij}}{r_o^{\pi\pi}} \right)^{p_{bo,6}} \right]$$



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.

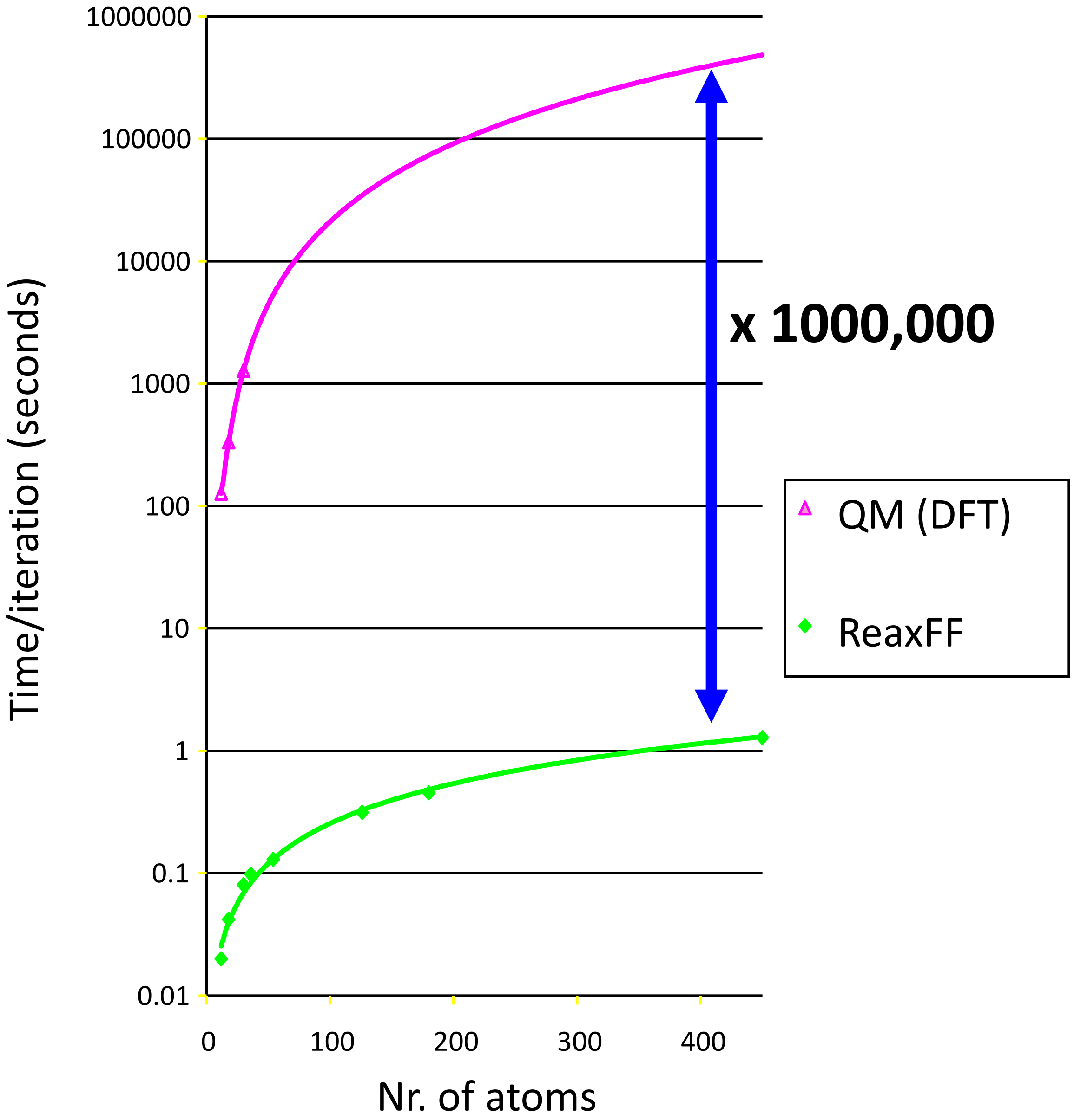
General Rules for ReaxFF

- 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

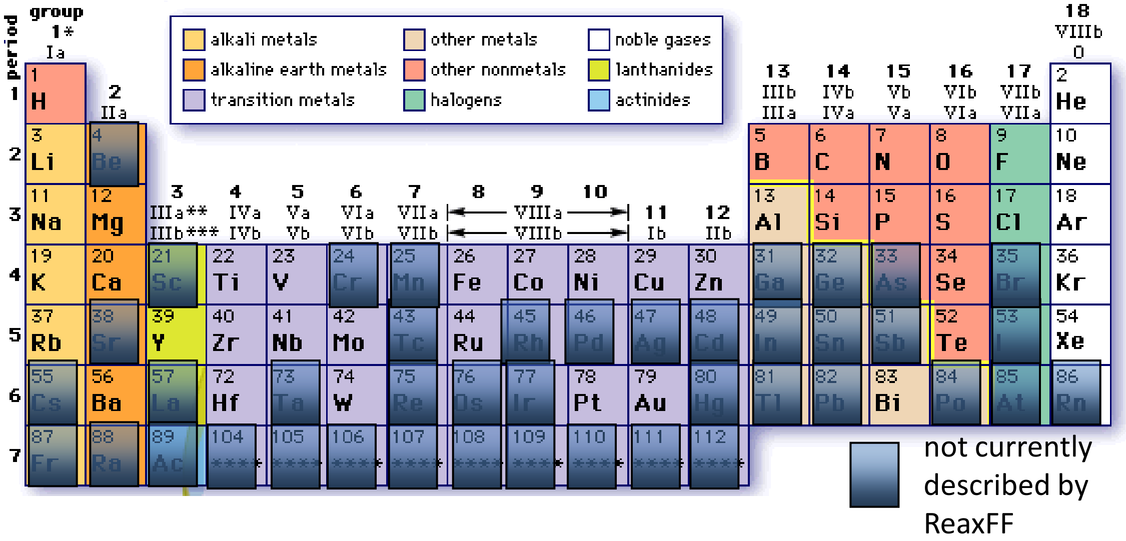


- ReaxFF allows for reactive MD-simulations on systems containing more than 1000 atoms
- ReaxFF is 10-50 times slower than non-reactive force fields
- Better scaling than QM-methods (NlogN for ReaxFF, N^3 (at best) for QM

Current Development Status of ReaxFF

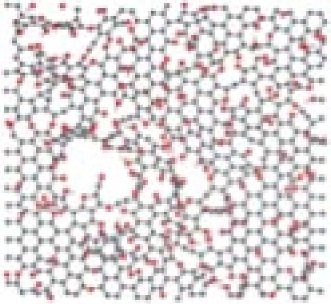
- ReaxFF combines covalent, metallic and ionic elements allowing applications all across the periodic table
- All ReaxFF descriptions use the same potential functions, enabling application to interfaces between different material types
- Code has been distributed to over 150 research groups
- Parallel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

ReaxFF transferability

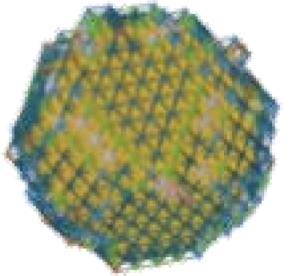


ReaxFF user community

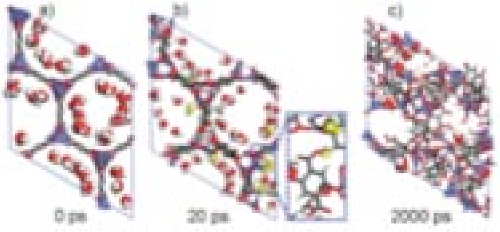
Name	Institute	Distribution date	Application
Adam Skelton	vanderBilt U.	June 2009	Silica/water
Aidan Thompson	Sandia National Lab	July 2005	Incorporation into GRASP
Albert To	U. Pittsburgh	March 2009	Al_2O_3-phase change
Alejandro Strachan	Purdue U.	August 2005	Ferroelectrics, Si-nanowires
Alexey Kaledin	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
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)



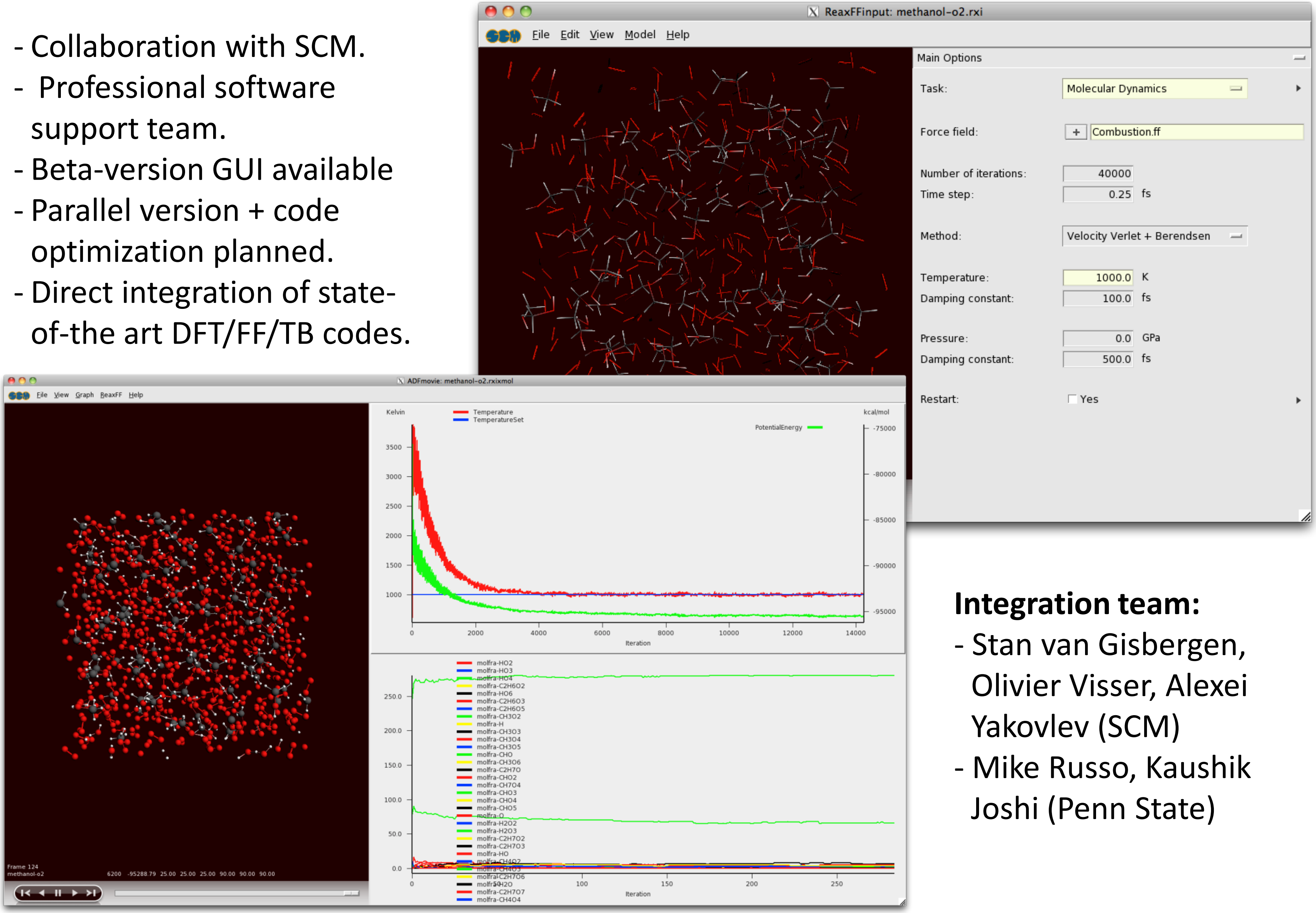
Annealing of gold nanoparticles (Keith et al., PRB 2010)



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



Main Options

Task: Molecular Dynamics

Force field: Combustion.ff

Number of iterations: 40000

Time step: 0.25 fs

Method: Velocity Verlet + Berendsen

Temperature: 1000.0 K

Damping constant: 100.0 fs

Pressure: 0.0 GPa

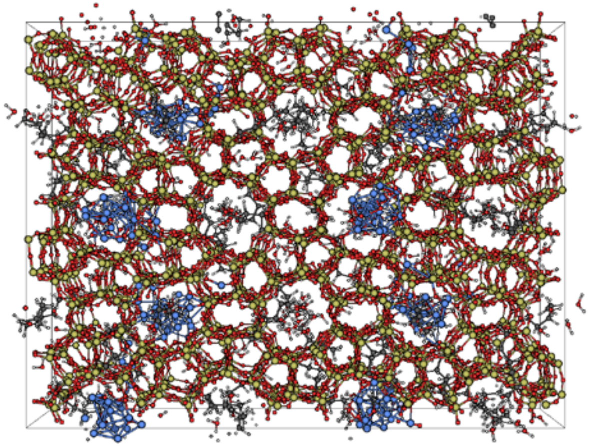
Damping constant: 500.0 fs

Restart: ☐ Yes

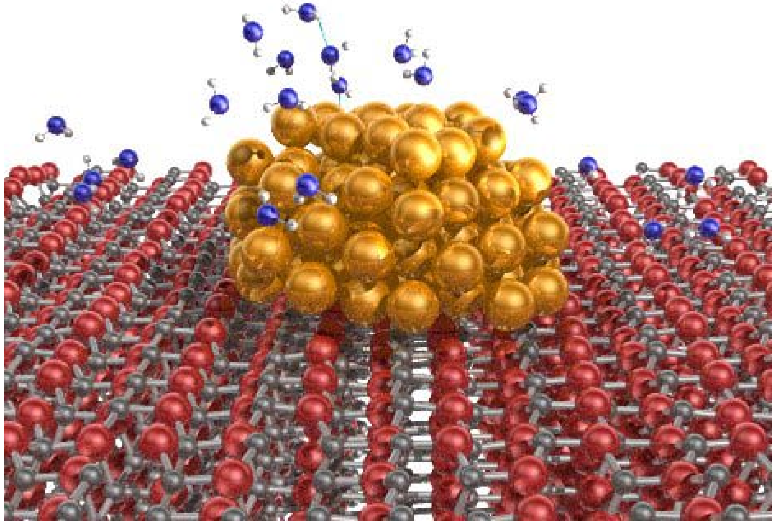
Integration team:

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

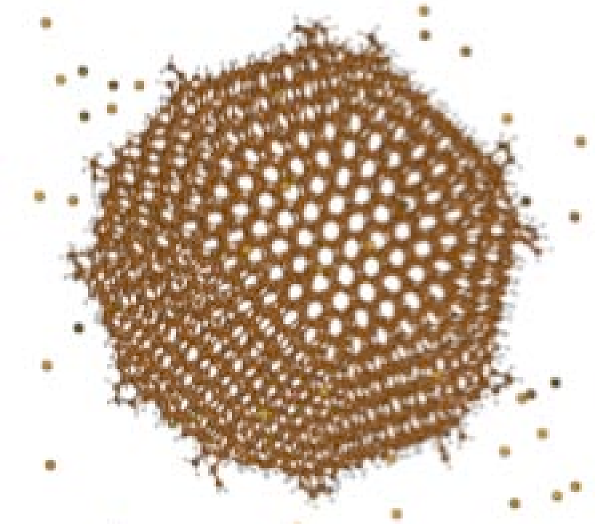
Examples of recent LAMMPS and ADF/ReaxFF simulations



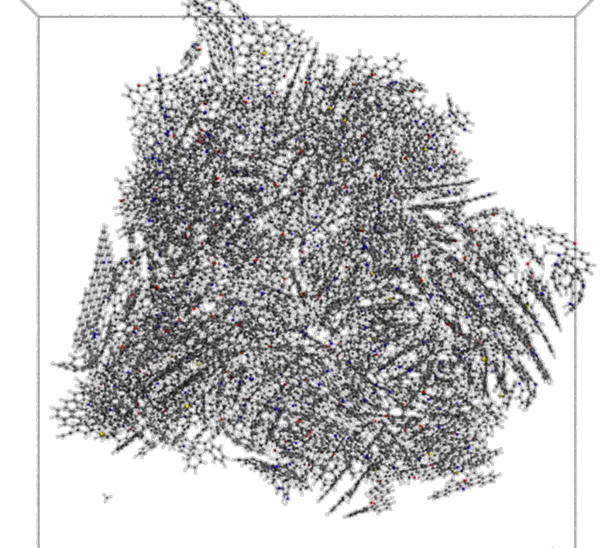
Hexane cracking on a Fe/H-ZSM5 catalyst (Fe/O: Aryanpour et al., JPC-A 2010)



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



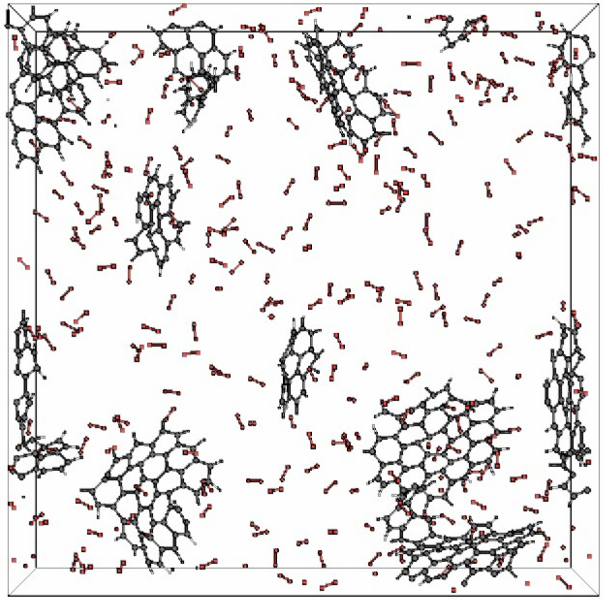
Noble gas accomodation coefficients on a graphene wafer (Kamat et al., submitted to JPC-A)



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

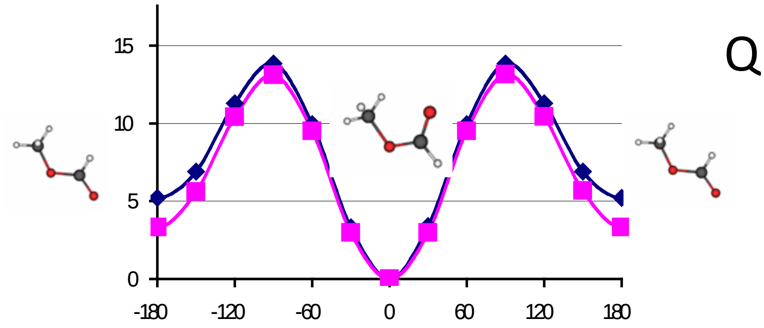
Outline

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



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

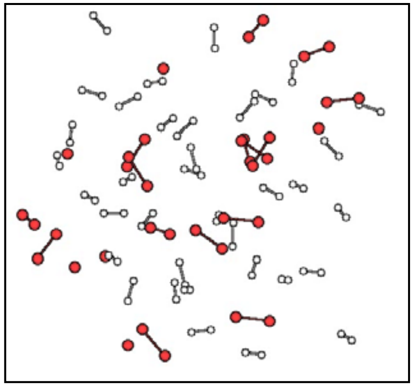
Combustion Reactions



QM

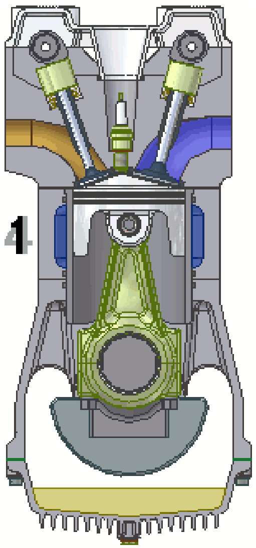
- Accurate energies for key reaction paths
- Size range: up to around 100 atoms
- Mostly static, highly limited dynamics

ReaxFF



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

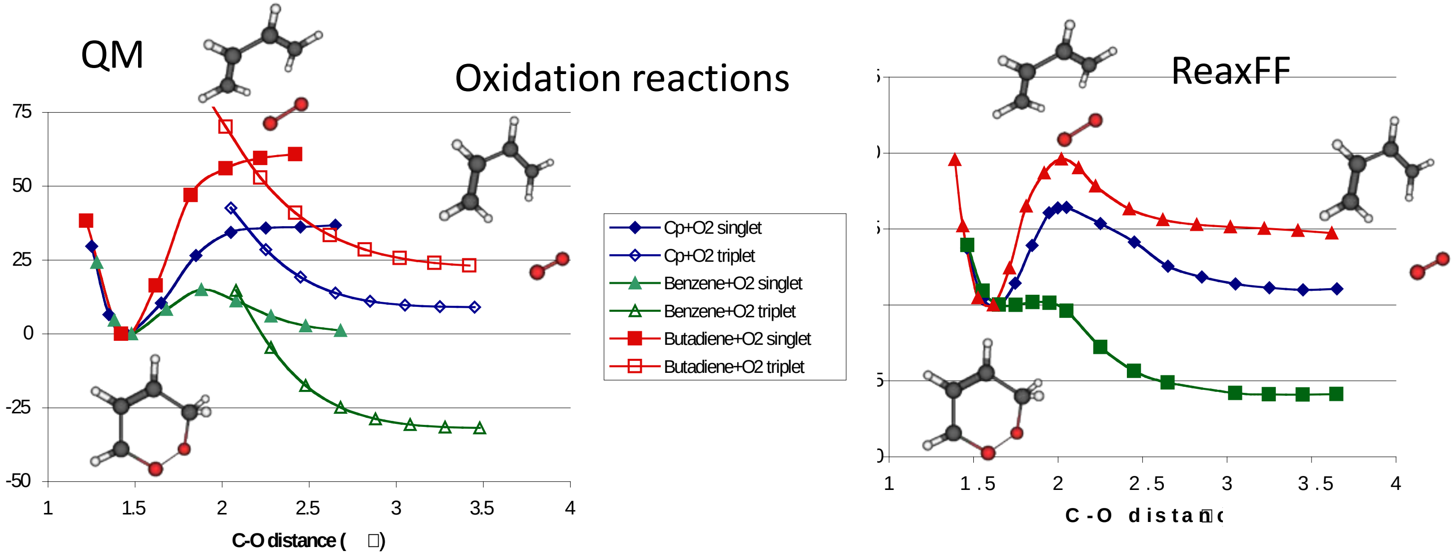
Engineering



Database of reaction kinetics and diffusion constants

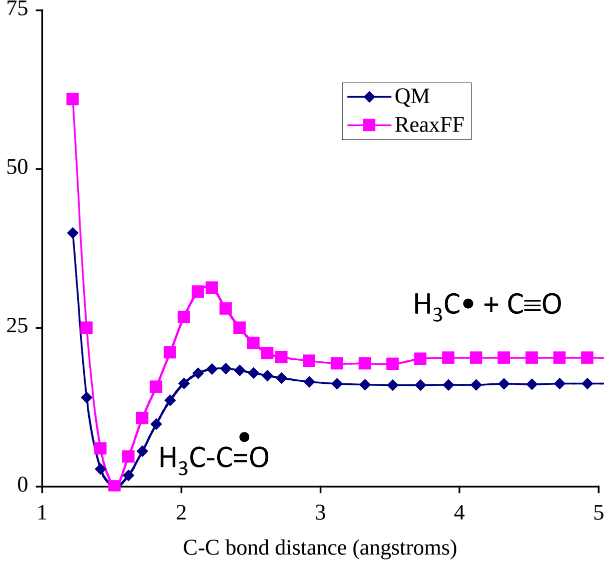
Force field development: hydrocarbon oxidation

Oxidation reactions

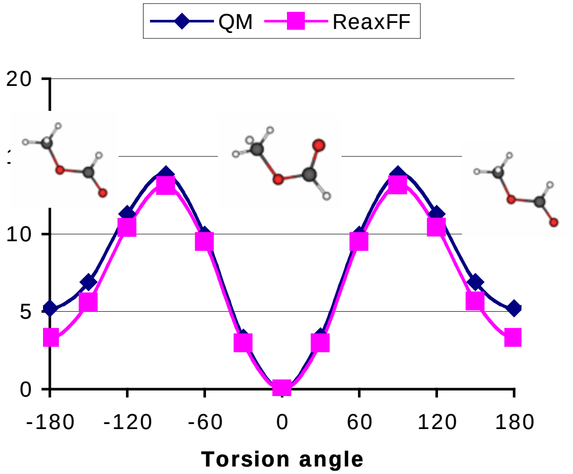


QM: Jaguar/DFT/B3LYP/6-311G**

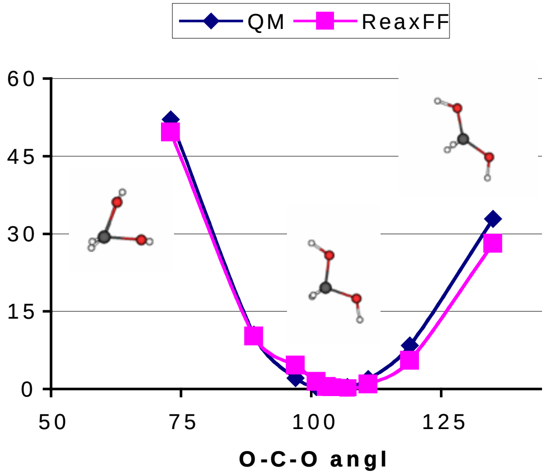
Radical rearrangements



Rotational barriers

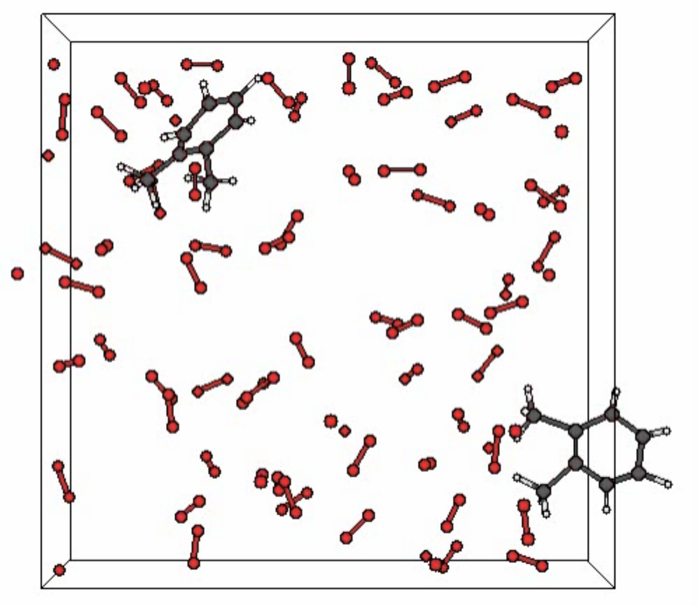


Angle strain

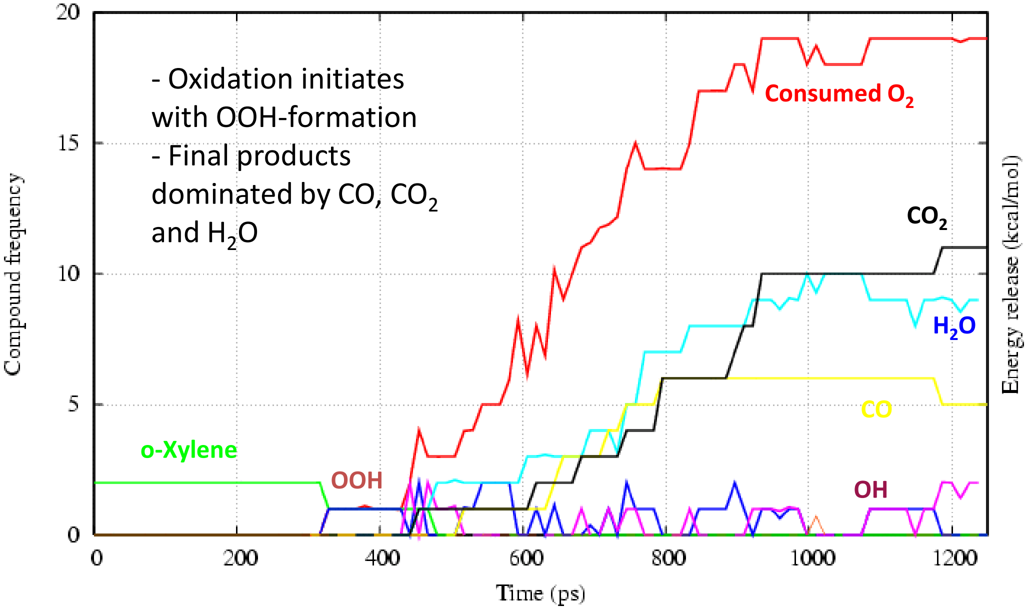


- total training set contains about 1700 compounds

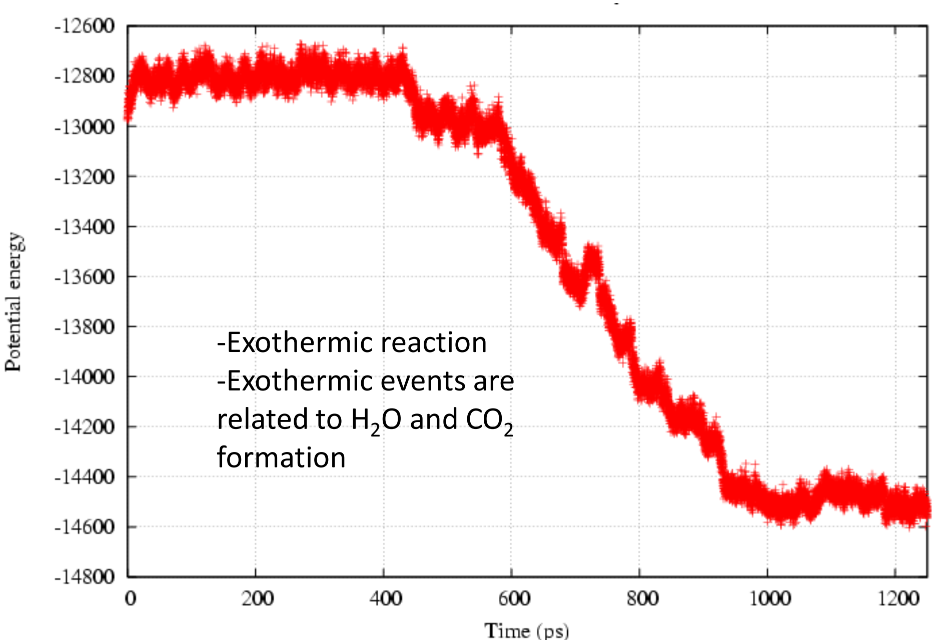
Test ReaxFF CHO-description: oxidation of o-xylene



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



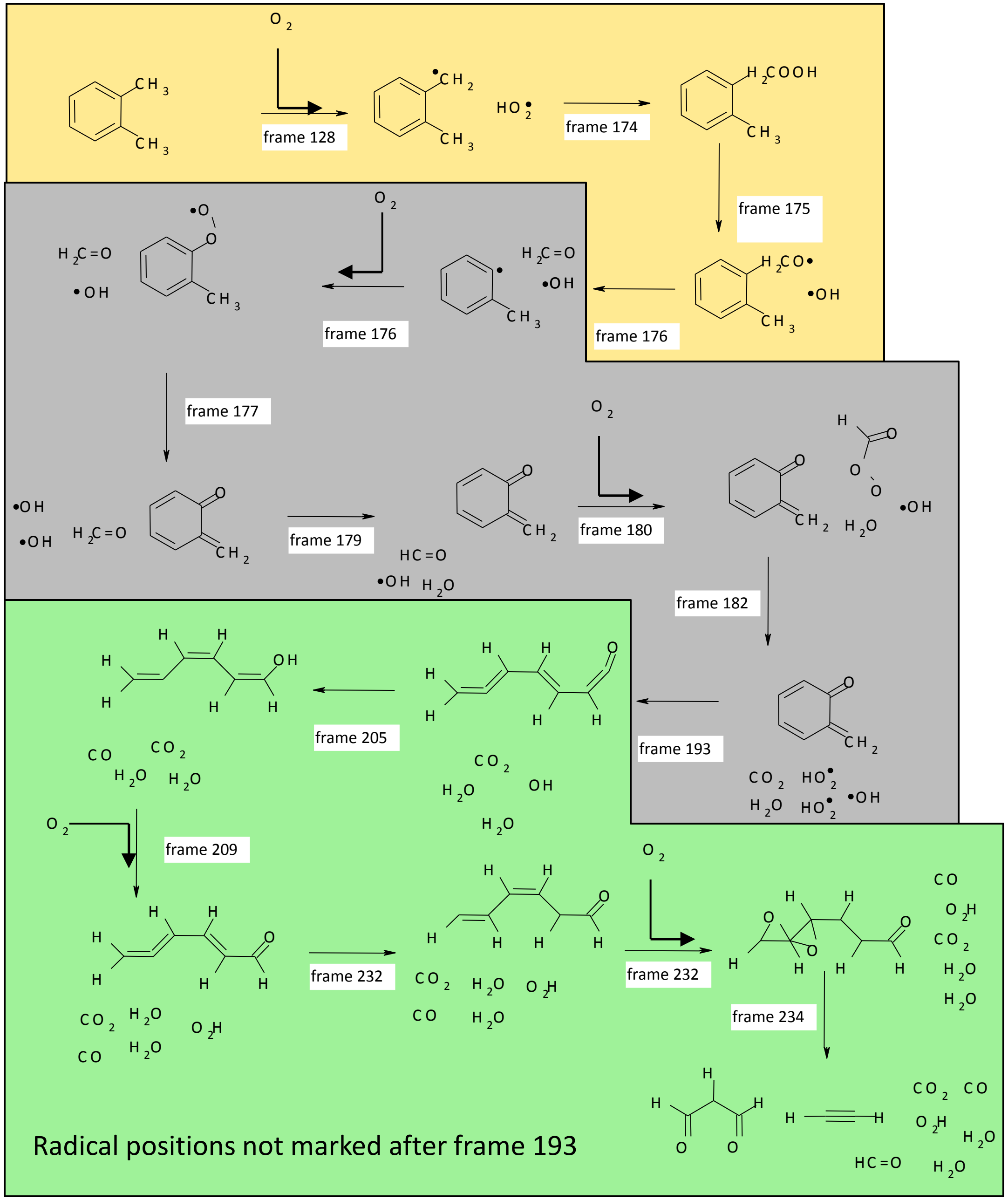
- Oxidation initiates with OOH-formation
- Final products dominated by CO, CO_2 and H_2O



-Exothermic reaction
-Exothermic events are related to H_2O and CO_2 formation

Chenoweth, van Duin and Goddard, JPC-A 2008

o-Xylene oxidation: Detailed reaction mechanism



Radical positions not marked after frame 193

- 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

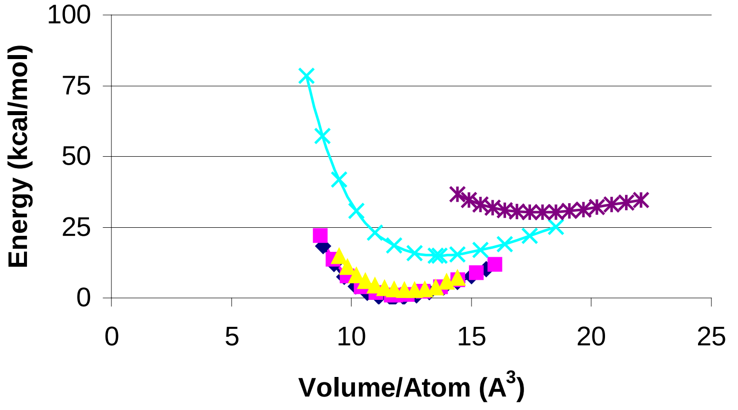
- **ReaxFF gives sensible predictions for the o-Xylene oxidation mechanism.**
- **This mechanism can be further validated against QM**

Development of a ReaxFF potential for Ni/S systems

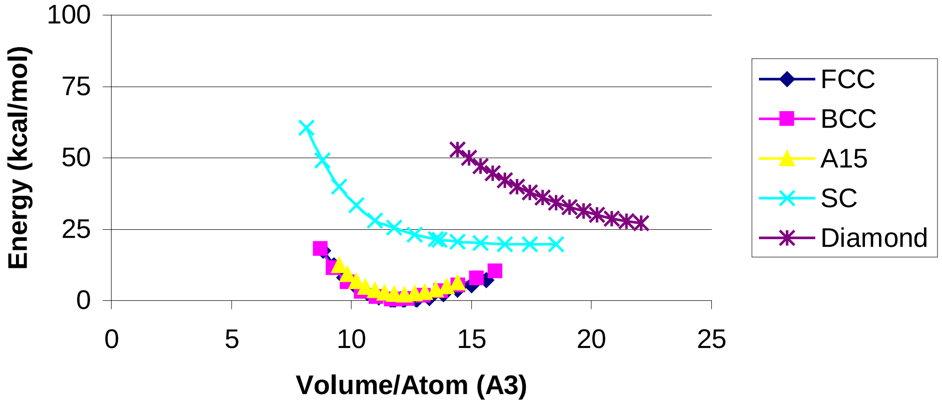
with Mu-Jeng Cheng, Yao Shao, Yi Liu, Bill Goddard and Tahir Cagin (Texas A&M)

Ni-bulk metal

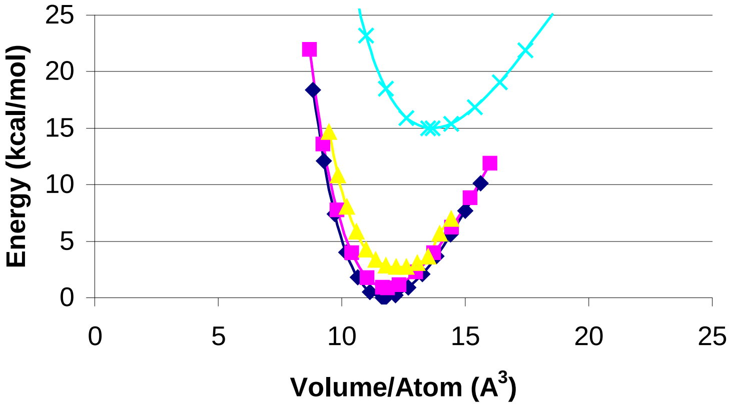
QC



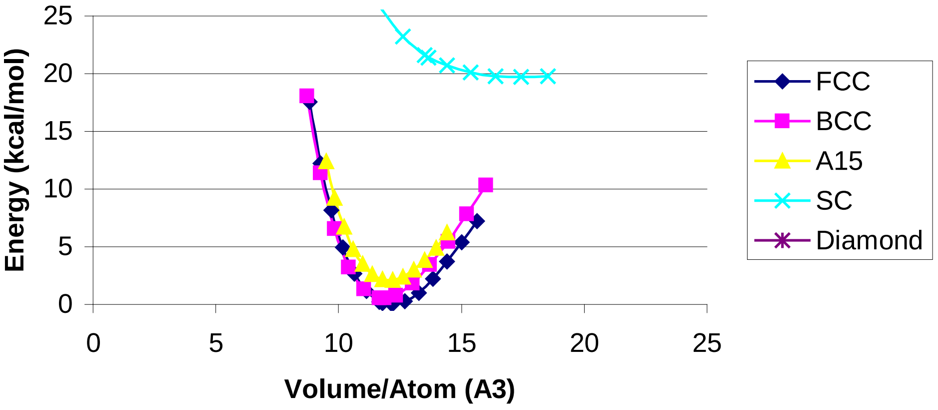
ReaxFF



QC

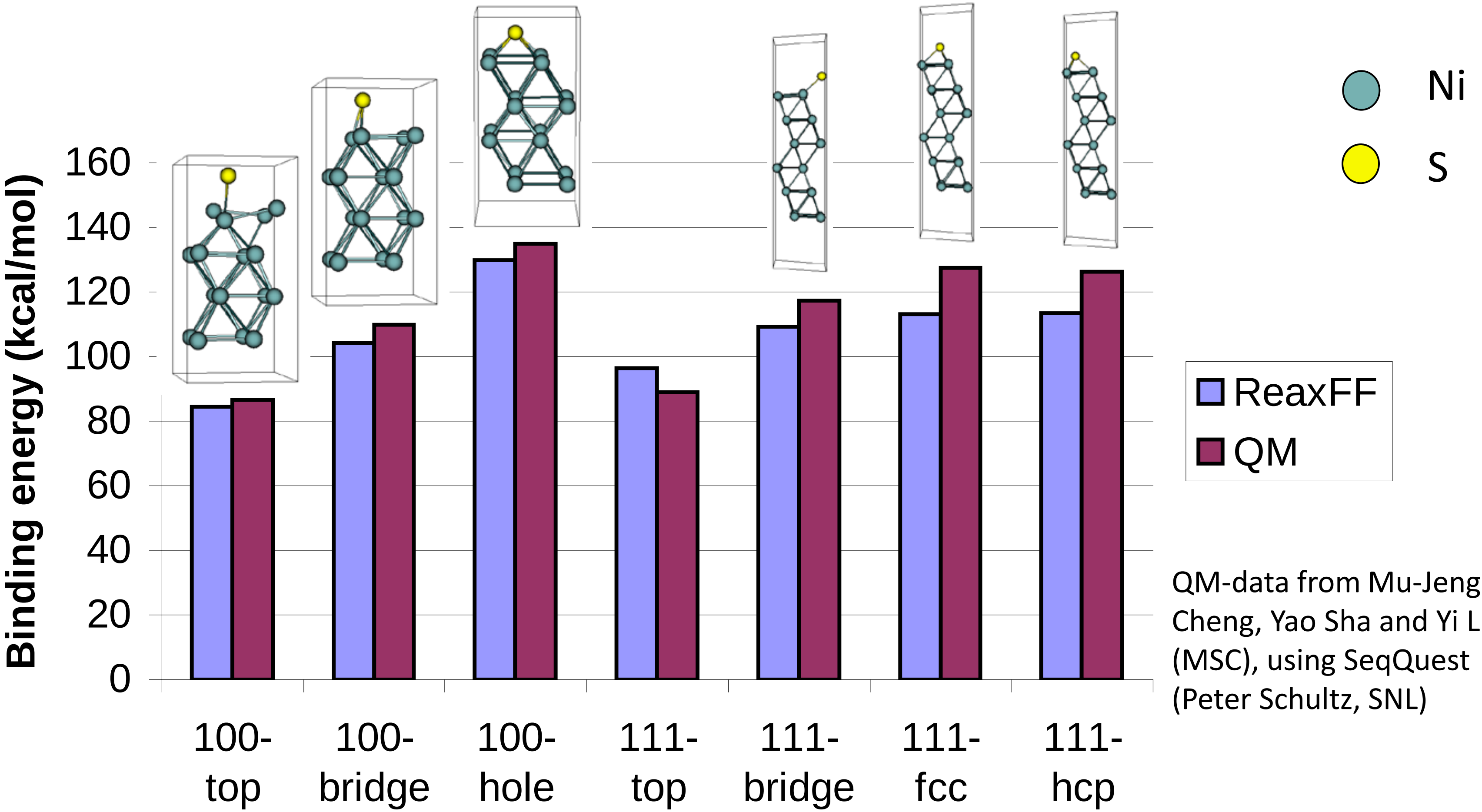


ReaxFF

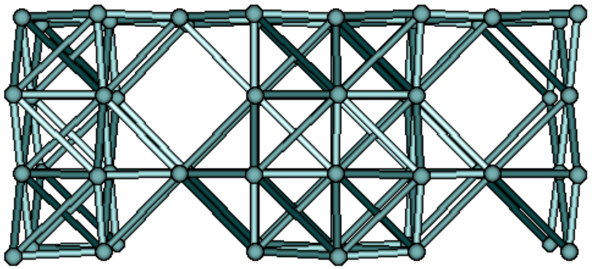


- Other data in training set: cohesive energy, surface energy (111 and 100), vacancy formation energy

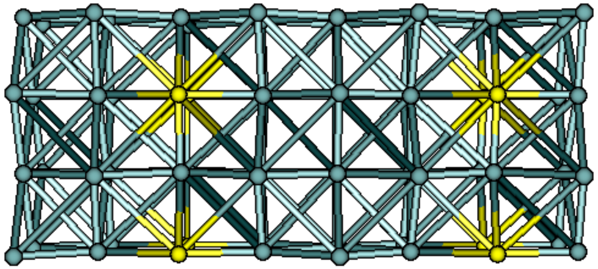
Sulfur binding energies to Ni-surface and subsurface sites



QM-data from Mu-Jeng Cheng, Yao Sha and Yi Liu (MSC), using SeqQuest (Peter Schultz, SNL)



Ni_7Vac_1

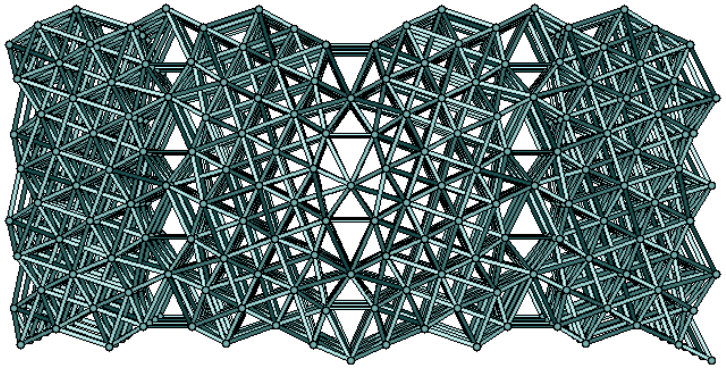


Ni_7S_1

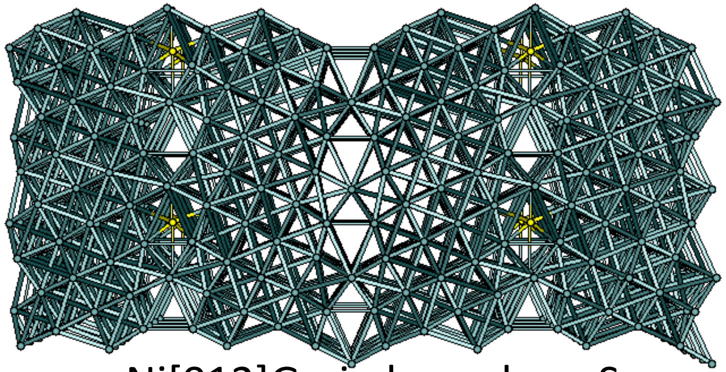
ΔE_{QM}=95.0 kcal/molS
ΔE_{Reax}=94.9 kcal/molS

- Sulfur strongly prefers surface-sites

Sulfur binding energies to Ni[012] grain boundaries



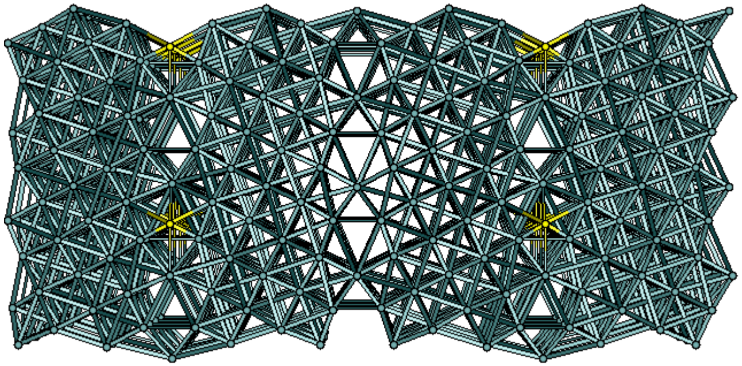
Ni[012]Grain boundary



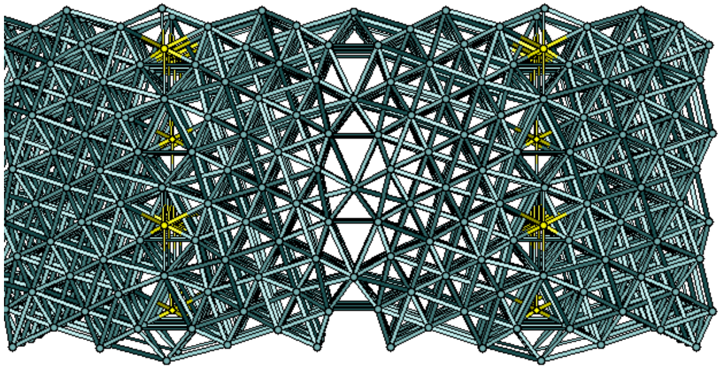
Ni[012]Grain boundary+S

● Ni

● S

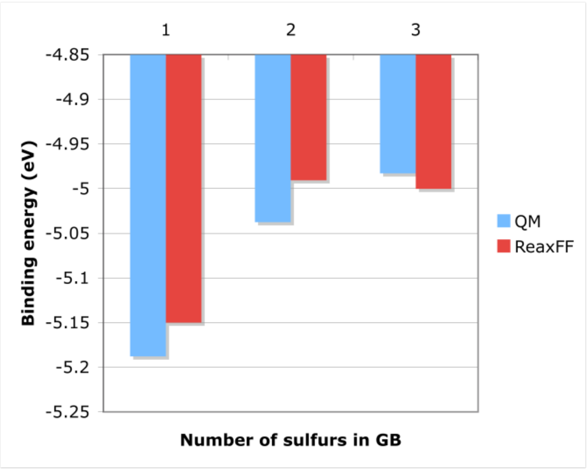


Ni[012]Grain boundary+2S



Ni[012]Grain boundary+3S

QM-data from Tahir Cagin-group (Texas A&M), parallel VASP

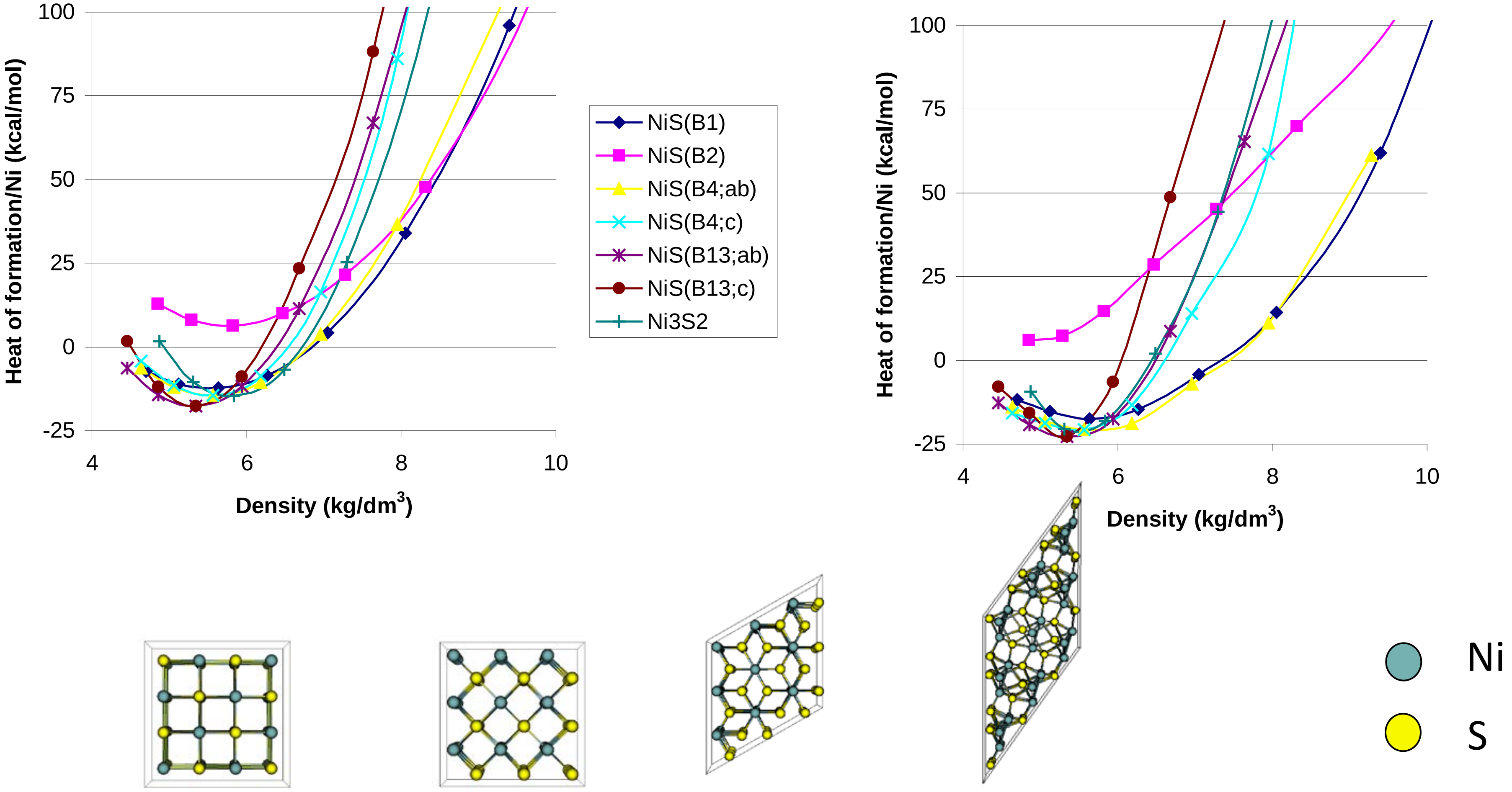


- Sulfur binding: surface>GB>bulk

NiS-bulk equations of state

QM

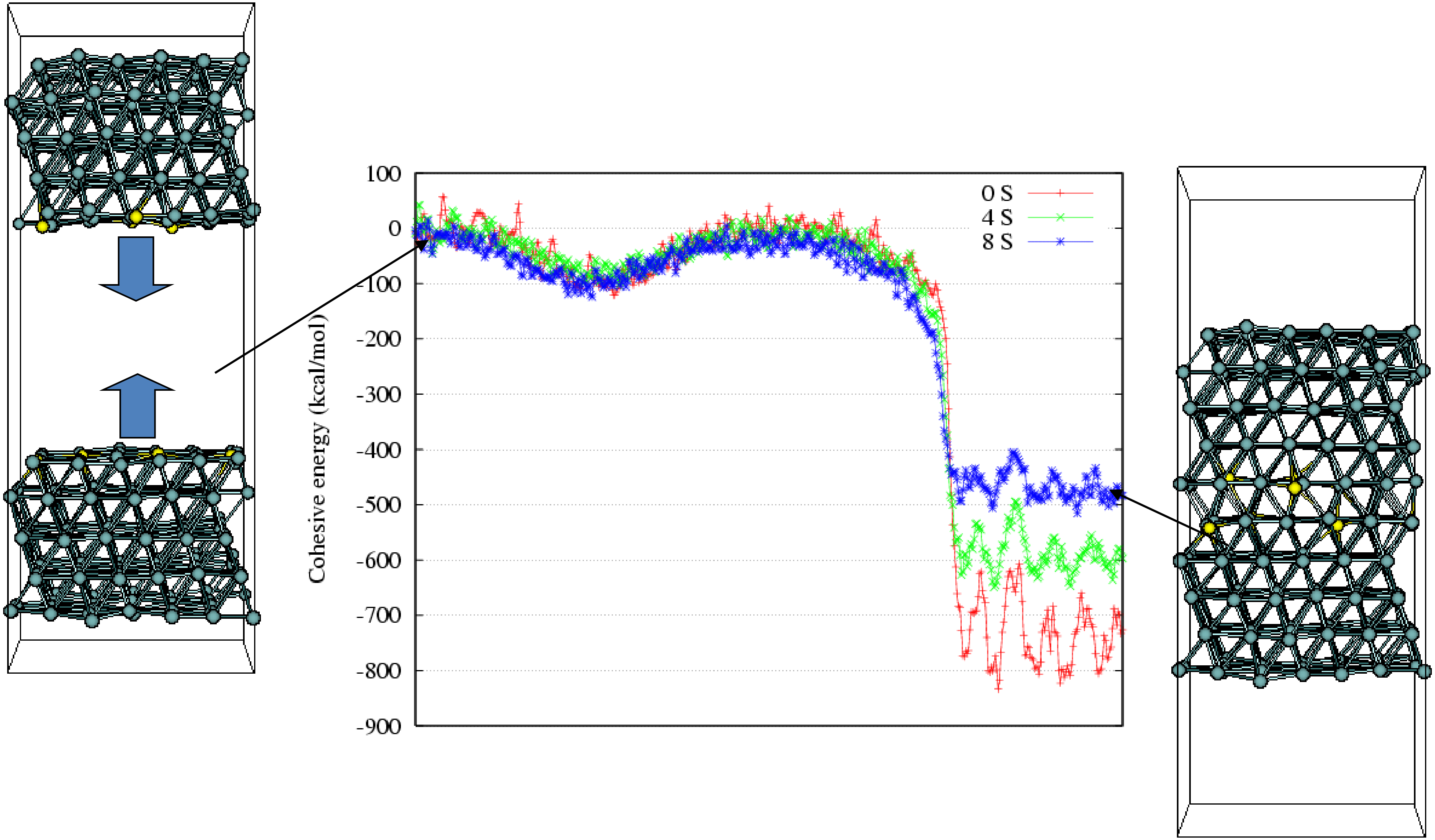
ReaxFF



NiS(B1) NiS(B2) NiS(B4) NiS(B13) Ni_3S_2

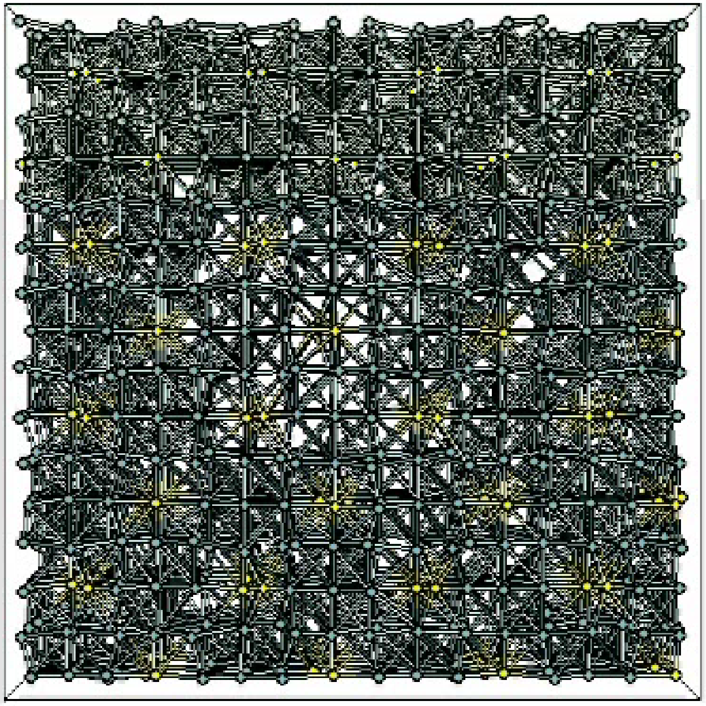
- ReaxFF is successfully tested against a wide range of Ni/S QM-data

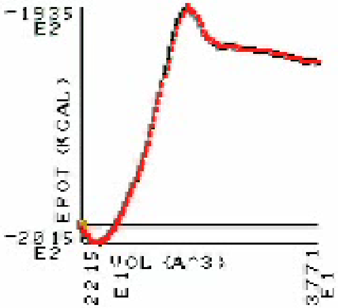
Simulations on cohesive energy as a function of S-coverage



- Surface sulfur greatly reduces cohesive energy

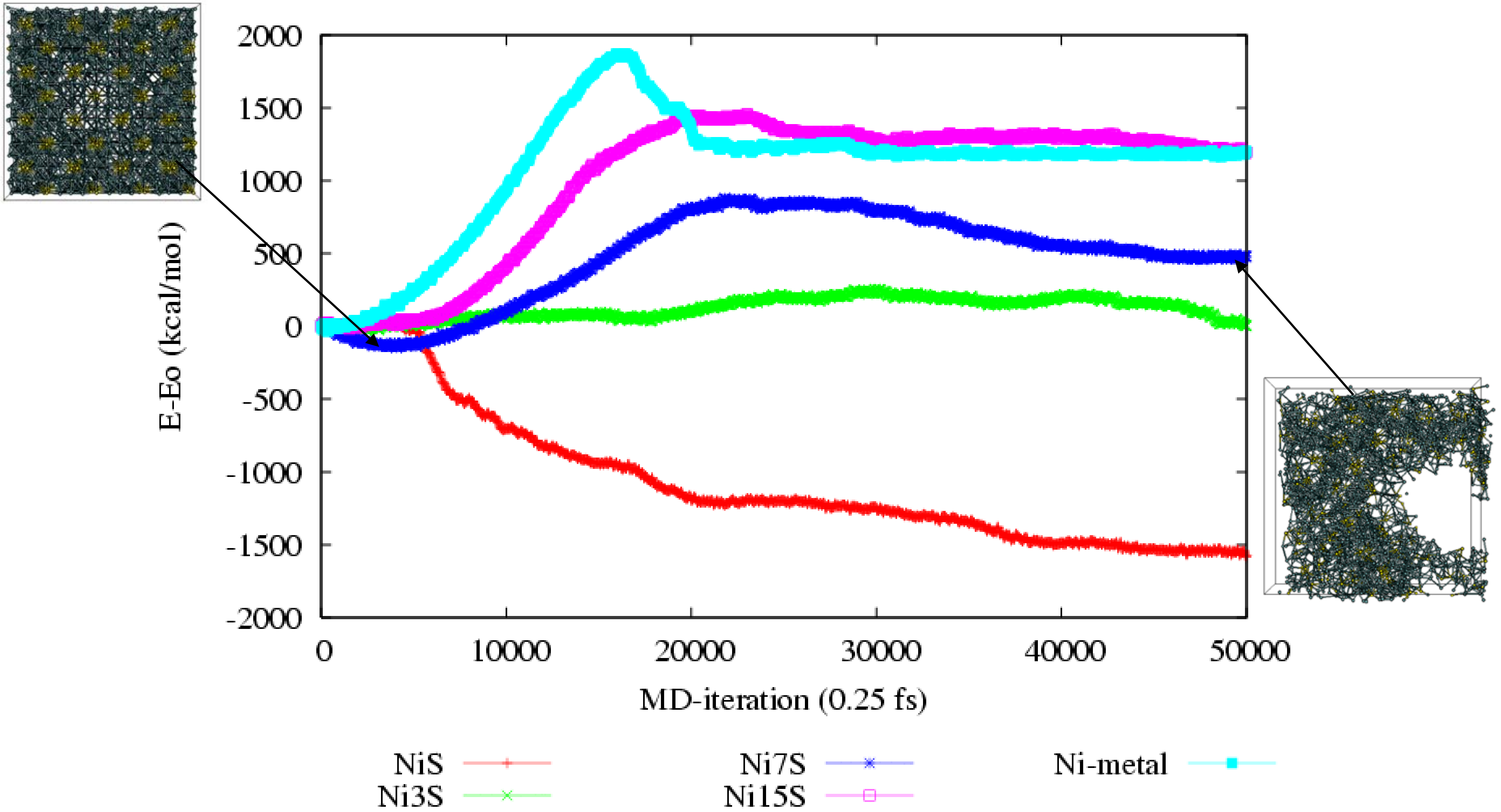
Simulations on material failure as a function of S-concentration





- Ni_7S-phase; expansion in 111-direction
- 2048 atoms; T=300K; NVT-simulation

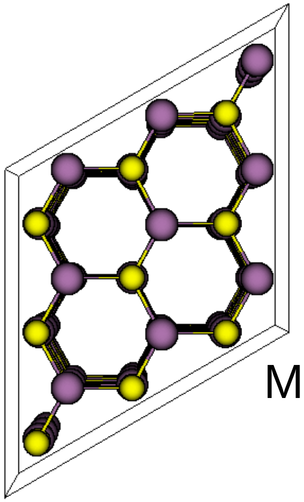
Simulations on material failure as a function of S-concentration



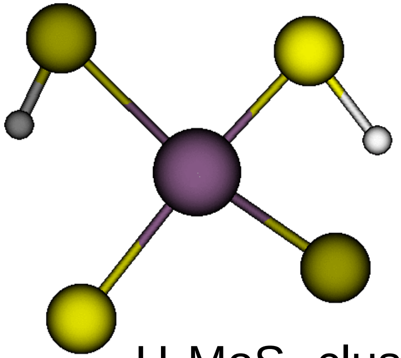
- Sulfur significantly weakens the material
- Surface formation becomes exothermic at high sulfur concentrations

REAXFF Mo/O/H_2S ReaxFF FORCE FIELD

- Initial Mo/O/H parameters are from Goddard 2008 (Topics in Catalysis 50, 2-18)
- Parameters were expanded to Mo/S/H interactions by fitting against the following DFT-cases
  - Mo-S and Mo=S bond dissociation in H_2MoS_4-cluster
  - S-S and S=S bond dissociation in H_2S and S_2
  - Equation of state and heat of formation of the MoS_2 hexagonal crystal
  - Charge distributions, bond lengths and valence angles for $Mo_xS_yH_z$-clusters



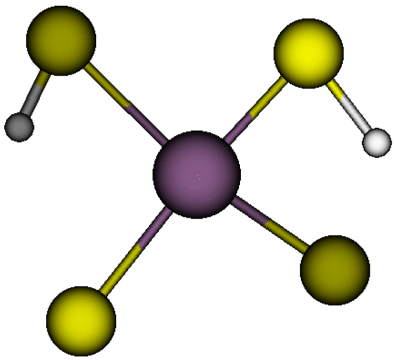
MoS_2 crystal



H_2MoS_4 cluster

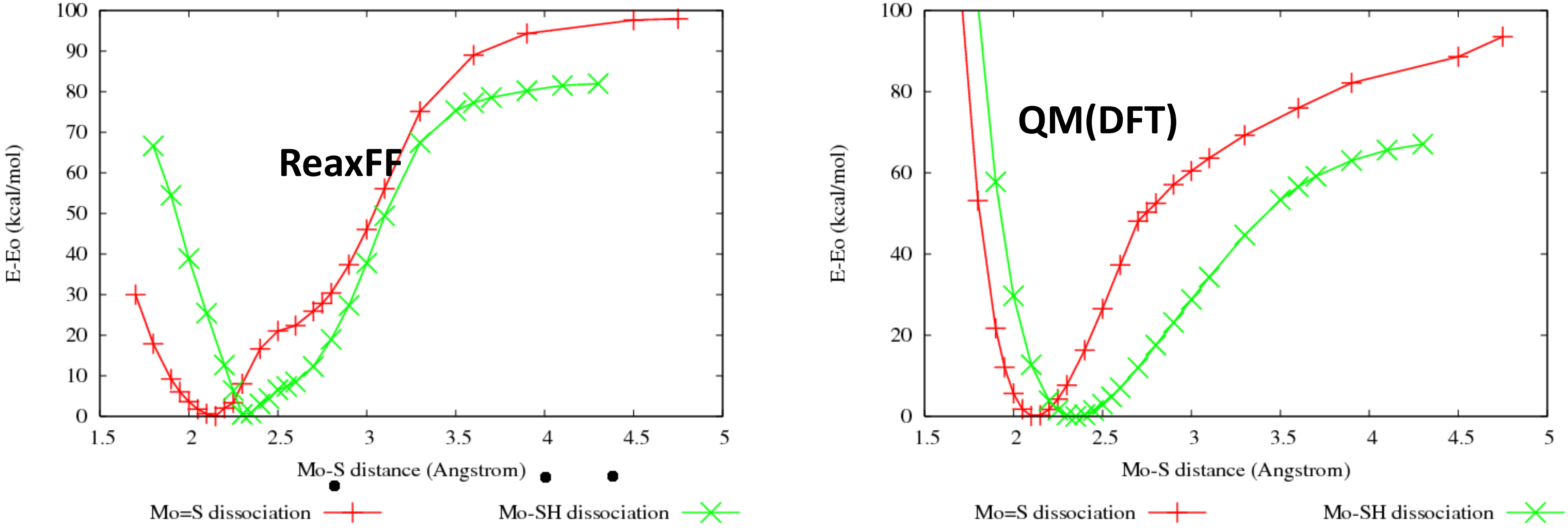
REAXFF Mo/O/H$_2$S ReaxFF FORCE FIELD (CONT.)

- ReaxFF reproduces shortening of Mo=S double bond relative to Mo-S single bond.
- ReaxFF reproduces increased dissociation energy of double bond and provides a quantitative accurate dissociation energy.
- ReaxFF does not fully reproduce the compressive behavior of the Mo-S bonds and gives a larger force-gradient around the equilibrium.

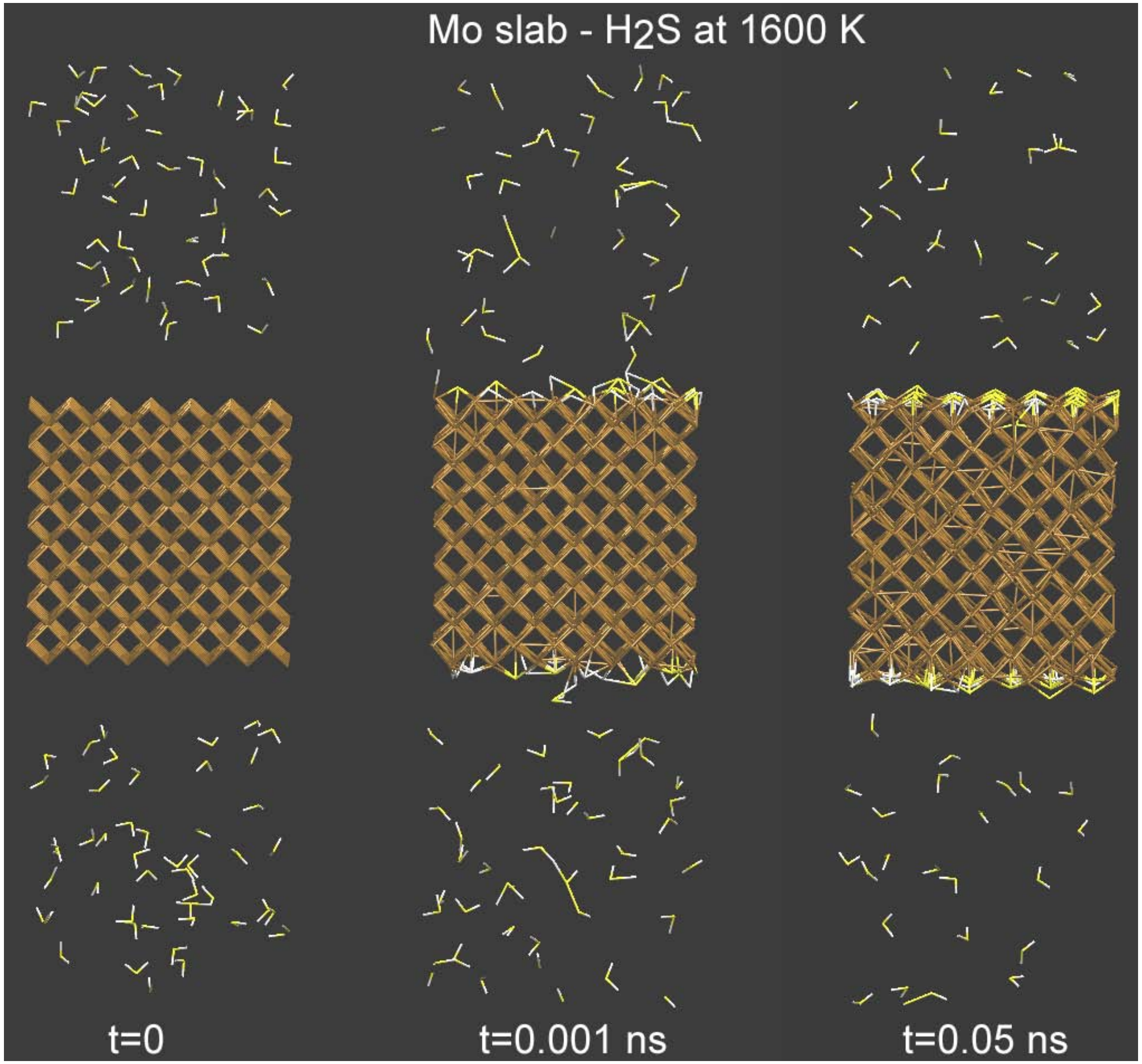


H_2MoS_4 cluster

Single- and double bond dissociation in H_2MoS_4-cluster

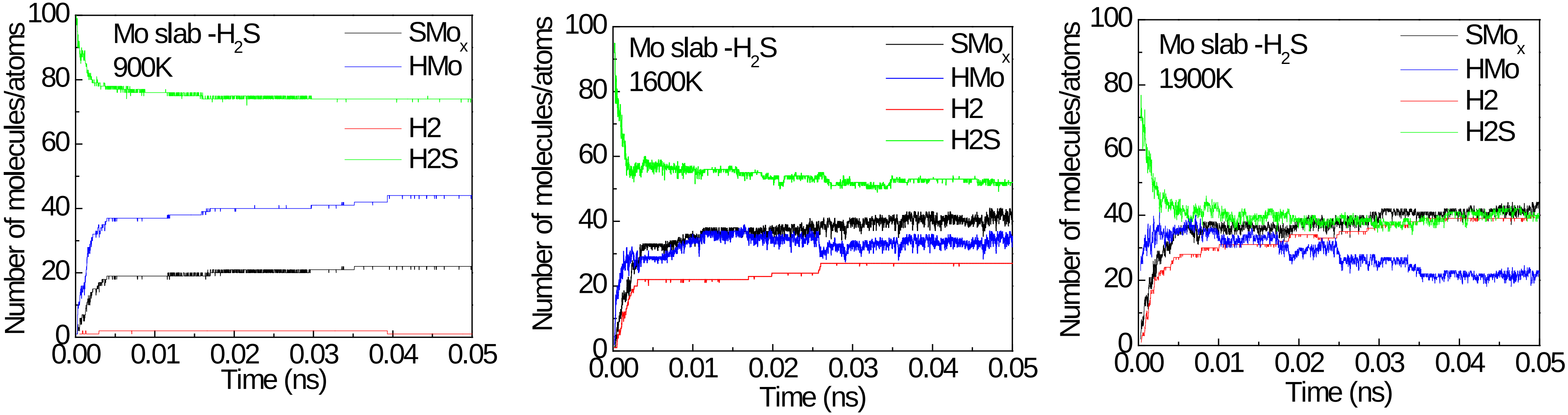


REAXFF MODELING OF Mo – H_2S INTERACTIONS



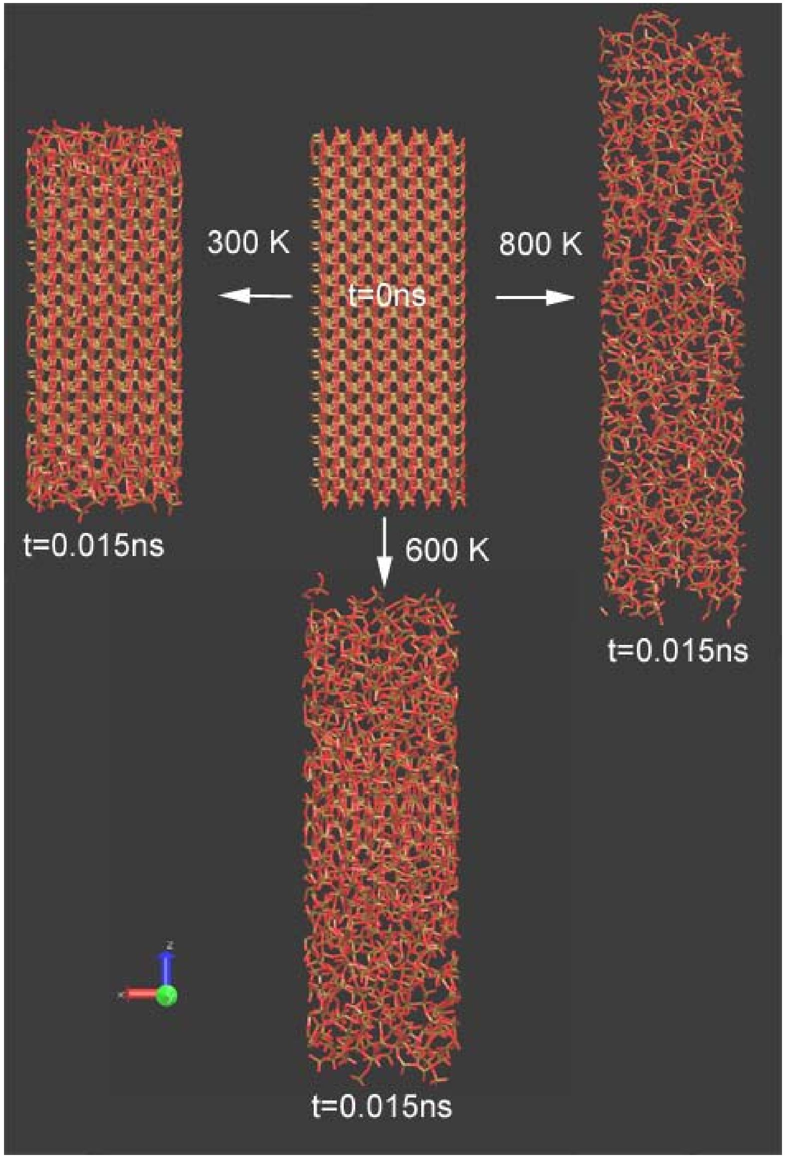
- Interactions of H_2S with Mo slab were modeled to test Mo-H_2S ReaxFF force field.
- H_2S diffused into the slab and decomposed there to form S and H.
- Mo-Mo metal bonds were replaced by S-Mo bonds leading to S agglomeration in the slab.
- H desorbed from Mo slab and formed H_2 in the gas phase.

REAXFF MODELING OF S AGGLOMERATION IN Mo SLAB



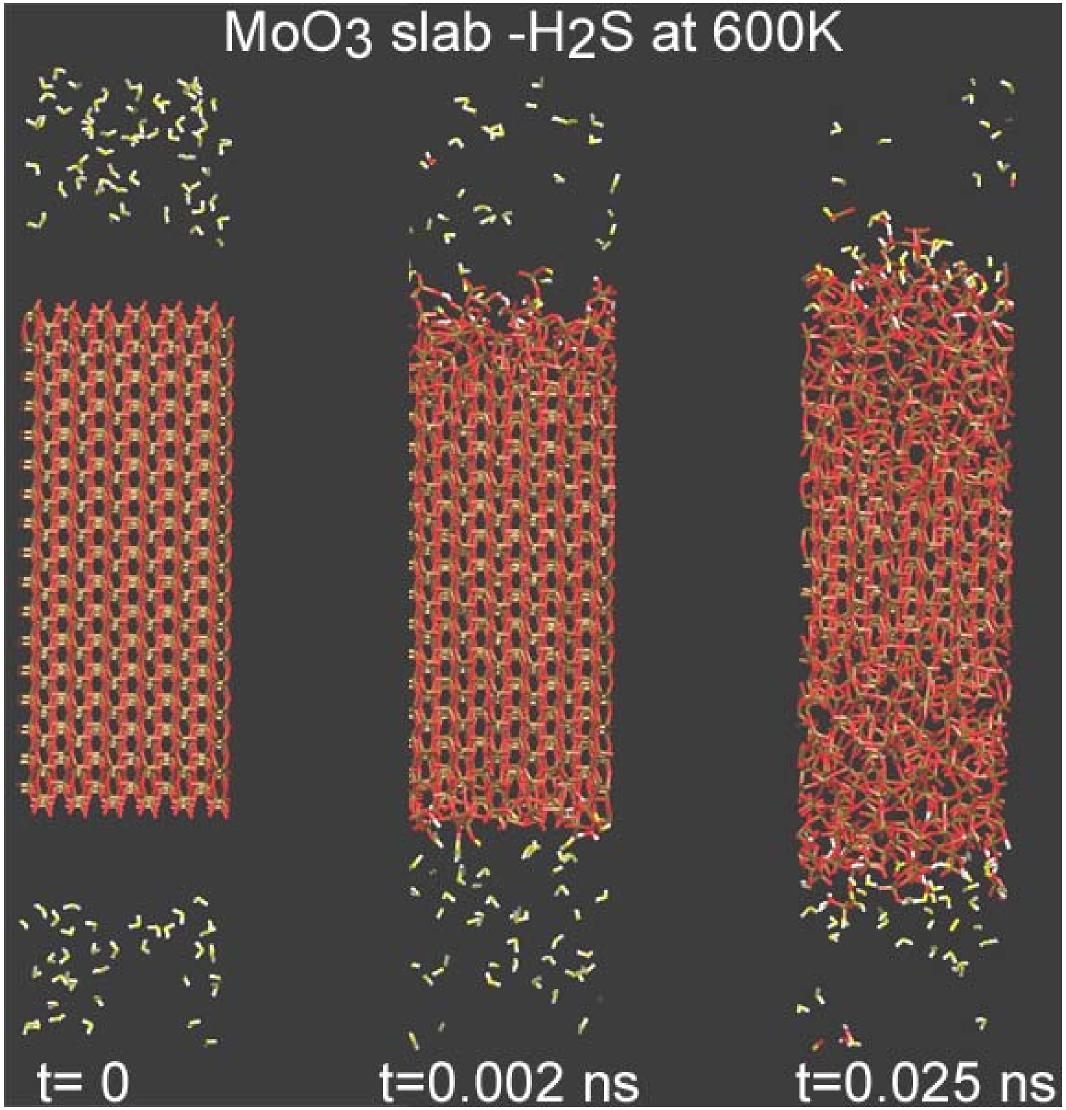
- **Initially, gaseous [H_2S] quickly decreases with an increasing time as H_2S readily absorbs onto Mo surface sites.**
- **Once surface sites are occupied, the rate of [H_2S] decomposition decreases and becomes steady.**
- **SMo_x concentration doubles as temperature increases from 900 K to 1600 K.**
- **A further temperature increase weakly affects SMo_x concentration indicating that S does not easily diffuse inside the Mo slab.**
- **At temperature below 1600 K, H resulting from H_2S decomposition preferably remains in the slab.**
- **As temperature increases above 1600 K, H concentration in the slab initially increases with time, reaches a peak value, and then decays as H increasingly desorbed from Mo slab to form gaseous H_2.**

REAXFF MODELING OF MoO_3 SLAB



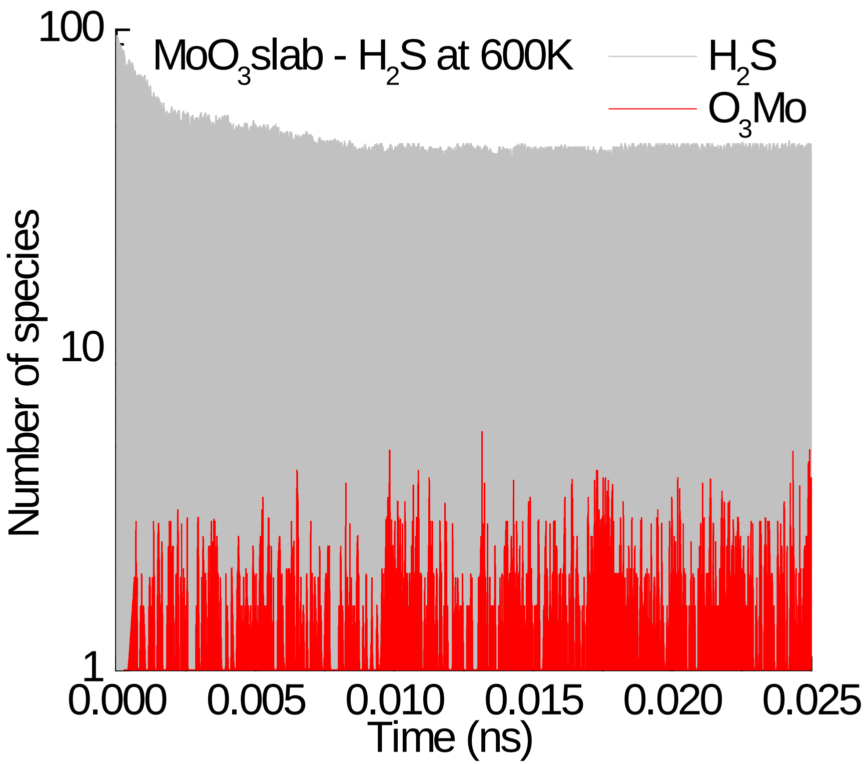
- Typical oxidation product that Mo forms is molybdenum trioxide (MoO_3).
- MoO_3 has a high vapor pressure and sublimes at substantial rates above 900 K, resulting in accelerated metal loss from the alloy.
- Set of simulations was performed using 3,000 atom MoO_3 slab to determine the transition from crystal to amorphous structure with increasing temperature.
- It was found that MoO_3 slab consists of crystal bulk structure and amorphous surface layer at temperature below 600 K.
- However, the slab has excessive amorphous soft phase at temperatures above 600 K (MoO_3 melting temperature is 1068 K).
- This deficiency will be fixed during future work by computing the larger set of QM data on crystalline and an amorphous MoO_3 structures and using this set to retrain ReaxFF force field.

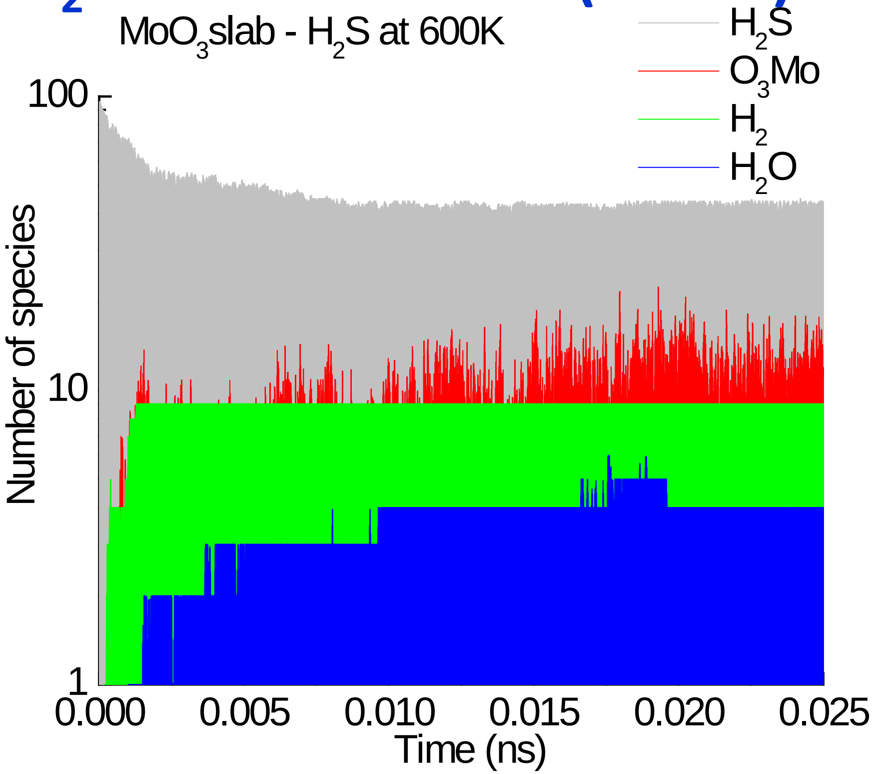
REAXFF MODELING OF MoO_3 – H_2S INTERACTIONS



- In slagging gasifier environment, metal oxide refractories are the base material instead of metal alloys.
- H_2S interactions with MoO_3 results in its decomposition and S agglomeration.
- 3,000 atom MoO_3 slab with 100 H_2S gaseous molecules was used to study the effect of sulfur agglomeration.

REAXFF MODELING OF MoO_3 – H_2S INTERACTIONS (CONT.)

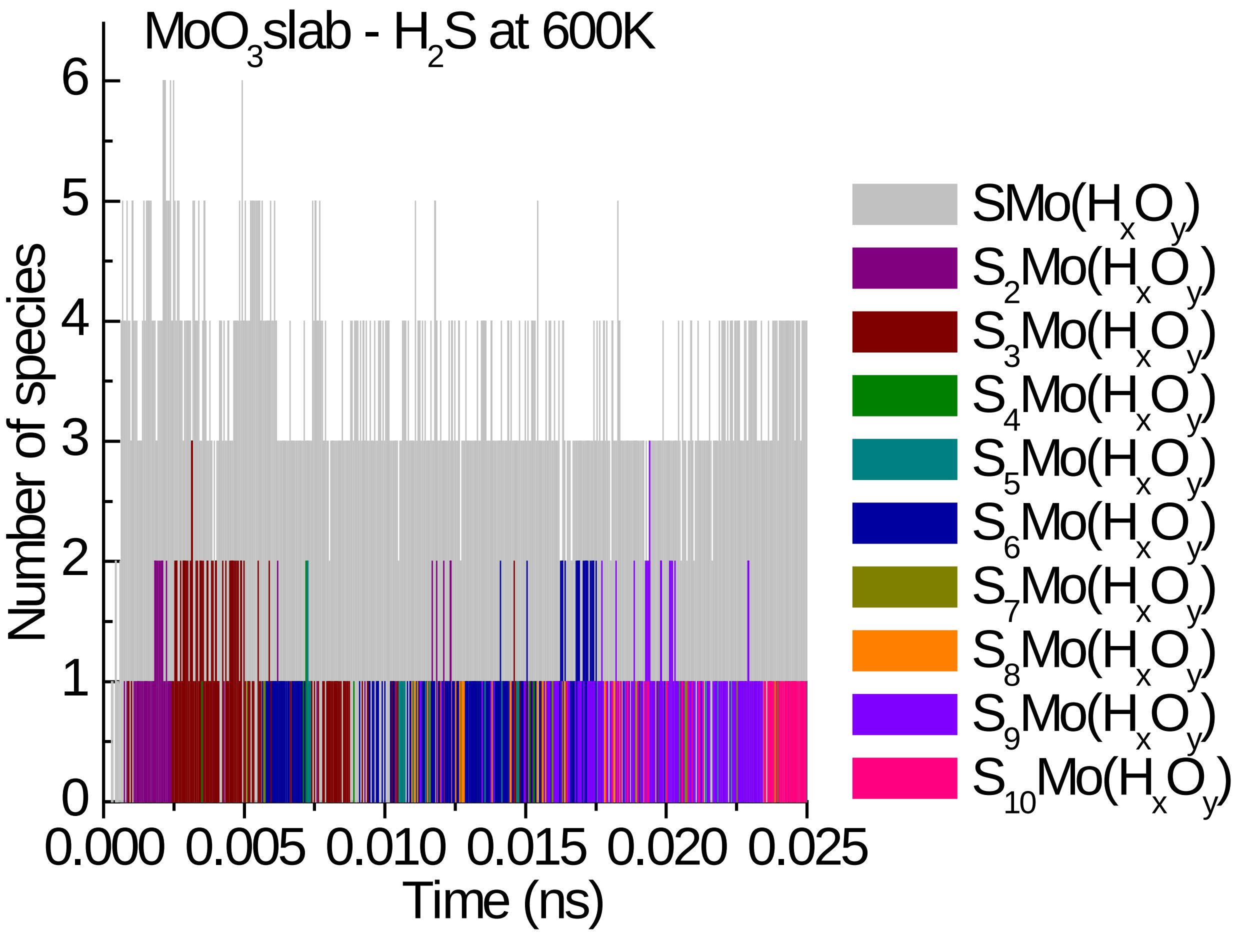




- **O_3Mo species were detected in the amorphous surface layer of the slab.**
- **H_2S diffuses into this amorphous layer and decomposes there to form H_2O and H_2 species.**

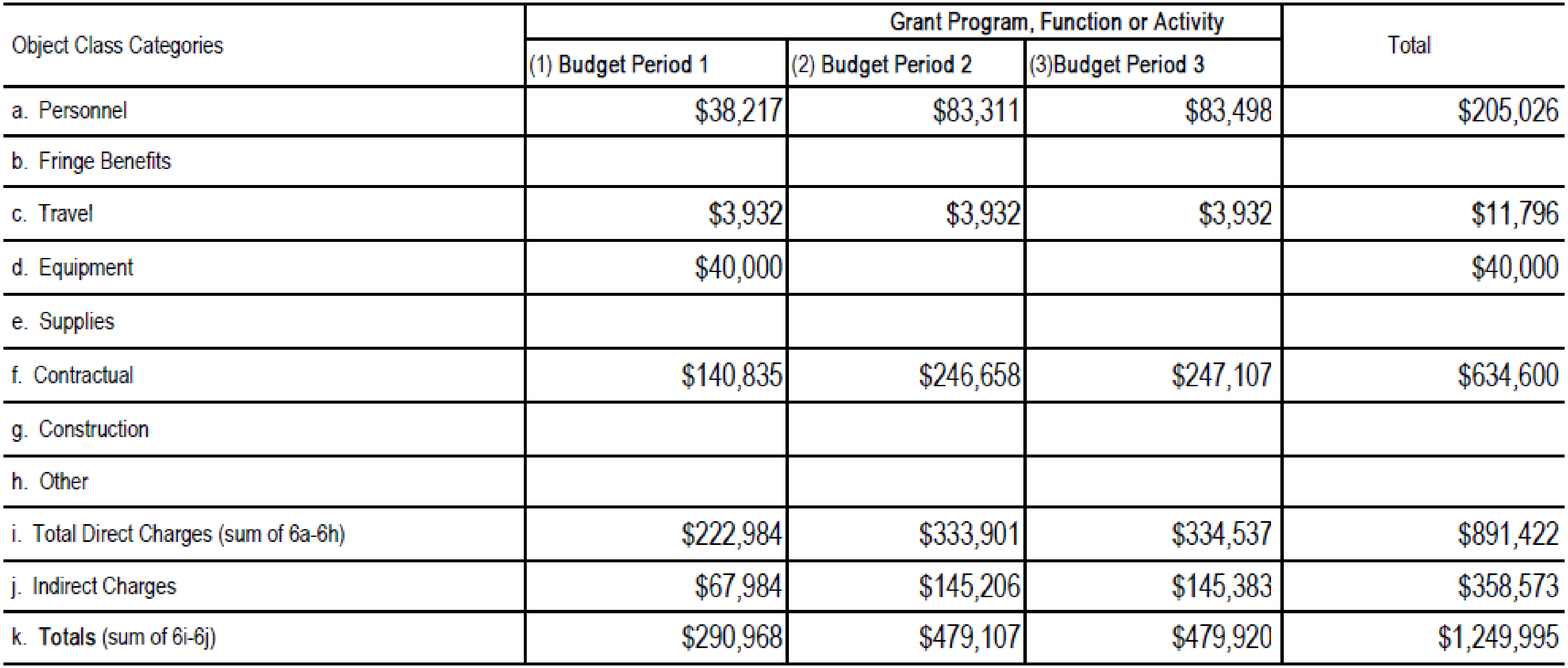
REAXFF MODELING OF S SEGREGATION IN MoO_3 SLAB

- **According to thermodynamics it is nearly impossible to replace oxygen – metal bonds by sulfur – metal bonds.**
- **As soon as surface amorphous layer with voids and cracks is formed, sulfur segregates to the fresh metal surface.**
- **Sulfur surface segregation decreases the metal surface energy.**



- **ReaxFF simulation results clearly show the tendency for sulfur segregation.**

PROJECT BUDGET AND SCHEDULE



Object Class Categories	Grant Program, Function or Activity			Total
	(1) Budget Period 1	(2) Budget Period 2	(3)Budget Period 3	
a. Personnel	$38,217	$83,311	$83,498	$205,026
b. Fringe Benefits				
c. Travel	$3,932	$3,932	$3,932	$11,796
d. Equipment	$40,000			$40,000
e. Supplies				
f. Contractual	$140,835	$246,658	$247,107	$634,600
g. Construction				
h. Other				
i. Total Direct Charges (sum of 6a-6h)	$222,984	$333,901	$334,537	$891,422
j. Indirect Charges	$67,984	$145,206	$145,383	$358,573
k. **Totals** (sum of 6i-6j)	$290,968	$479,107	$479,920	$1,249,995

- **During year one, the feasibility of the proposed approach will be demonstrated.**
- **During year two, ReaxFF potentials for chromia and alumina based refractories will be developed and validated.**
- **In the third year, mechanisms of grain boundary segregation in slagging gasifier refractories will be determined and approaches to limit this segregation will be identified.**

PROJECT MANAGEMENT PLAN

- The project will be executed by CFDRC and PSU.
- CFDRC highly experienced manager Dr. Vernon Cole will provide program management.
- Dr. Alex Vasenkov (CFDRC) and Prof. Adri van Duin (PSU) co-Principal Investigators will coordinate activities with the team members.
- The decision-making process in this project is separated as follows:

  Dr. Vasenkov: overall project goals, assisted by the external consultants

  Prof. van Duin: ReaxFF force field development and applications.
- President of CFDRC Dr. Ashok Singhal and highly experienced consultant Dr. Brian Gleeson will act in advisory roles with regards to the overall program direction and any adjustments to the work plan arising at go/no-go decision points.

PROJECT RISKS AND THEIR MITIGATION

- There are manageable risks associated with the proposed research and development.
- Most notably, we recognize that the size- and time-ranges of the atomistic simulations do not yet provide a seamless match with the experimental resolution.
- In the case of large mismatch in simulation and experimental resolution, we will employ complementary computational tools including accelerated MD, kinetic Monte Carlo, and parallel replica methods.
- Simulations will be directed toward in-depth understanding of fundamental mechanism of segregation at the grain boundary.
- Another technical risk is in the development of Quantum Mechanics based ReaxFF potentials for chromium, the major element missing from the current library of ReaxFF potentials for simulations of refractories.
- The risks associated with this development are mitigated by
  - ➢Reported ReaxFF descriptions for a number of elements in the periodic table closely related to chromium, including molybdenum and vanadium,
  - ➢Proven strategy for the ReaxFF potential development, and
  - ➢Clearly defined individual steps in the development plan.

PROJECT RISKS AND THEIR MITIGATION (CONT.)

- Given the complexity of the interactions at the grain boundary of chromia and alumina based refractories, we anticipate that the initial ReaxFF force fields will make unexpected, and possibly erroneous predictions.
- We will validate these initial force field predictions by performing QM-based analysis of reaction energies and barriers associated with the ReaxFF-predicted processes.
- This QM/ReaxFF feedback loop will be continued until the high-temperature ReaxFF predictions are fully validated by QM calculations.
- On the whole, we are confident that the probability for the success of the proposed research is very high.
- This assessment is based on the proven expertise of CFDRC in materials modeling and 20 years experience in managing projects of similar size and complexity, as well as Prof. Adri C.T. van Duin's demonstrated expertise in the development and application of ReaxFF potentials.

MANAGEMENT PROCEDURES ON DECISIONS AND CONFLICT RESOLUTION

- It is expected that conflicts and disagreements can be avoided through the structures of individual task assignments.
- When disagreements arise, they can be resolved by the relevant team or through discussions between team leaders.
- In the exceptional case that a conflict cannot be resolved in this way, an External Management Committee may be called upon by a PI and asked to help in resolving the dispute or to present a solution.
- The External Management Committee will make a final decision, if necessary, by weighted voting.
- This decision is then binding to all management bodies.
- All pending conflicts will be solved within reasonable time frames.

PROJECT STATUS

- Get awarded with the complementary project for using CNMS computing facilities at ORNL (Proposal ID: CNMS2011-020, “Predictions of Grain Boundary Interactions Contributing to Degradation of Refractory Alloys“, February 1, 2011- January 31, 2012).
- Statement of Project Objectives is finalized.
- Penn State: PhD-student (Osvalds Verners) and postdoc (Mike Russo) have been hired (started Spring 2011).
- Assembly of ReaxFF potentials for Fe-Ni-Al_2O_3/S interactions begun.