

Development and applications of ReaxFF reactive force fields for combustion, catalysis and material failure

Adri van Duin

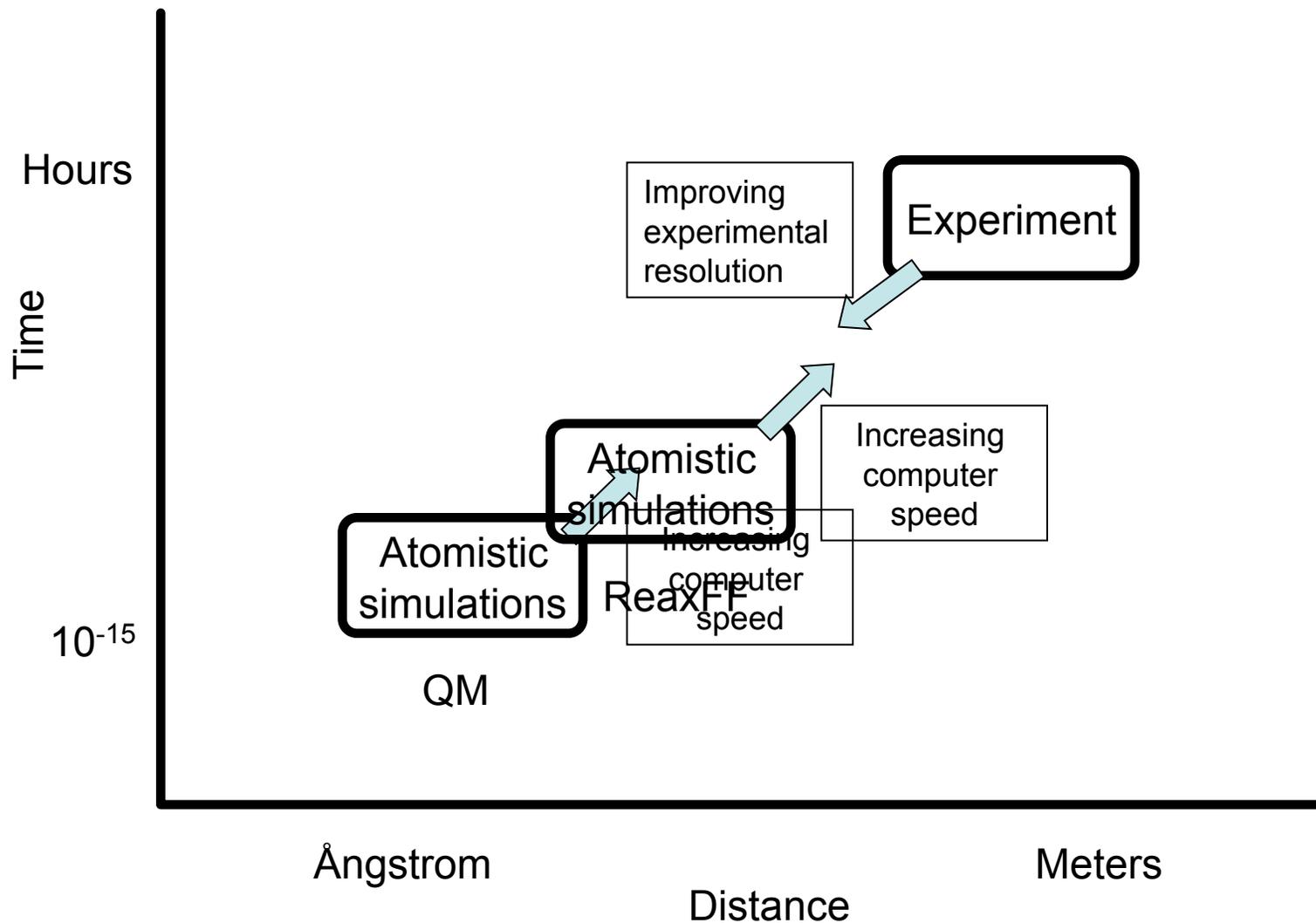
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NIST 2010 Workshop on Atomistic Simulations for
Industrial Needs, July 27

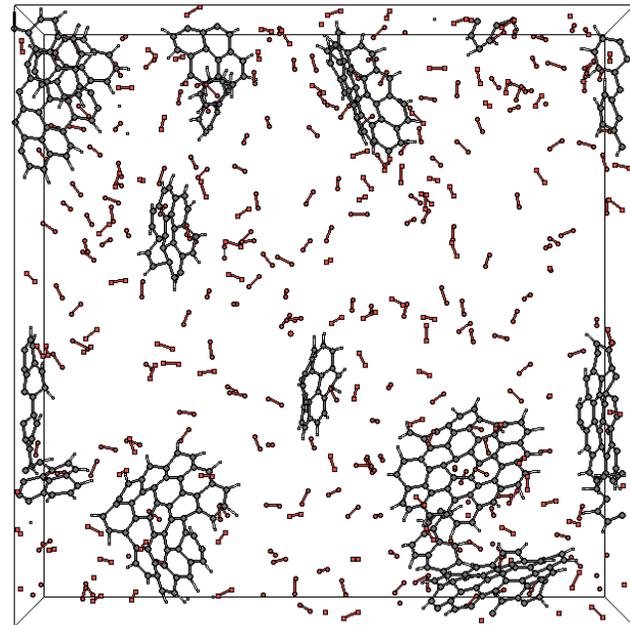


Solving the size/time gap between simulation and experiment



Outline

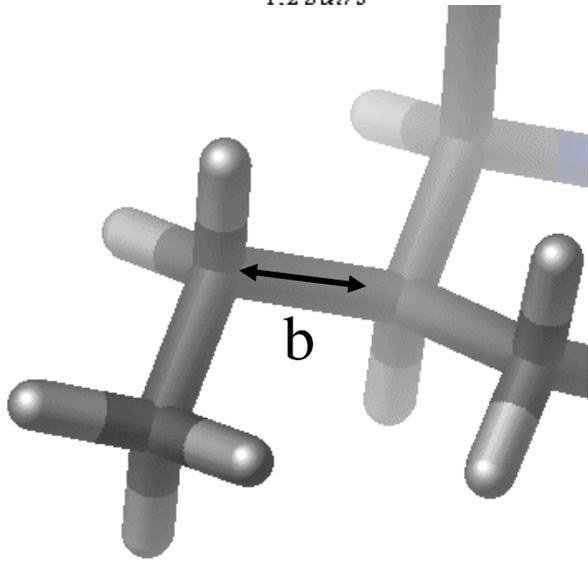
- Simulations on the dynamics of chemical reactions
- The ReaxFF reactive force field
- Overview of ReaxFF applications
 - Combustion reactions
 - Material failure
 - Catalysis
- Summary



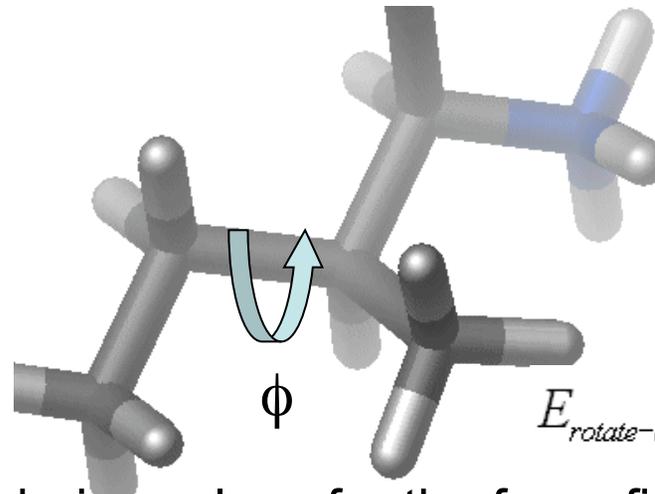
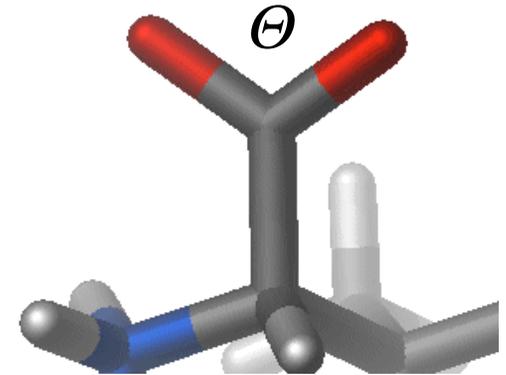
ReaxFF MD-simulation on soot combustion at elevated oxygen pressure. Soot structure provided by Jonathan Matthews (Penn State)

Force field methods

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



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



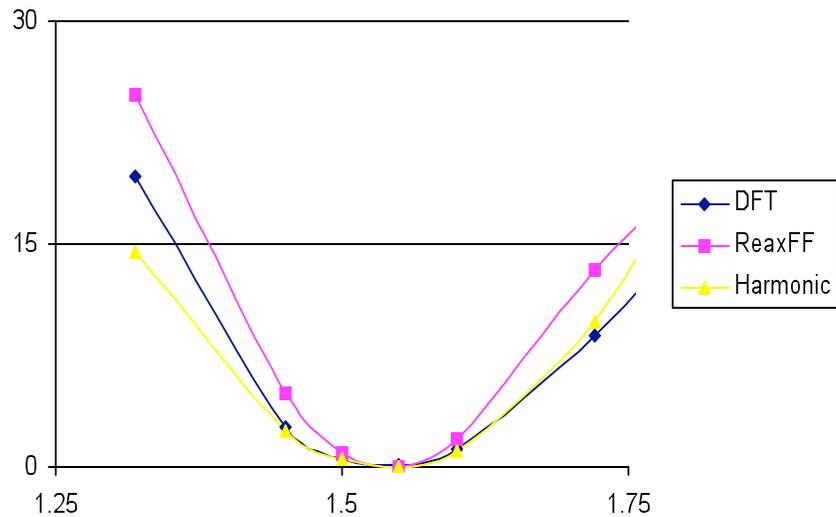
$$E_{\text{rotate-along-bond}} = \sum_{1,4 \text{ pairs}} K_\phi (1 - \cos(n\phi))$$

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

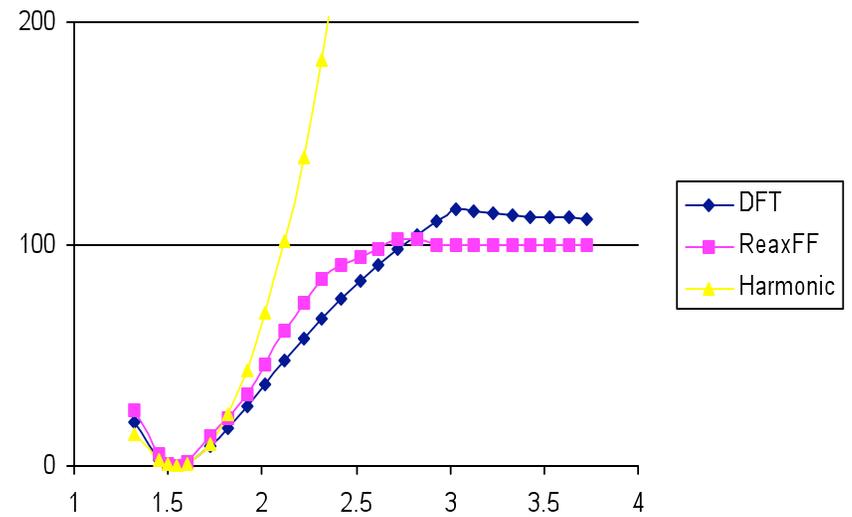
Failure of the harmonic model

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.

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

-To get a smooth transition from nonbonded to single, double and triple bonded systems ReaxFF employs a bond length/bond order relationship [1-3]. Bond orders are updated every iteration.

-All connectivity-dependent interactions (i.e. valence and torsion angles) are made bond-order dependent, ensuring that their energy contributions disappear upon bond dissociation [4].

- Nonbonded interactions (van der Waals, Coulomb) are calculated between **every** atom pair, irrespective of connectivity. Excessive close-range nonbonded interactions are avoided by shielding [4].

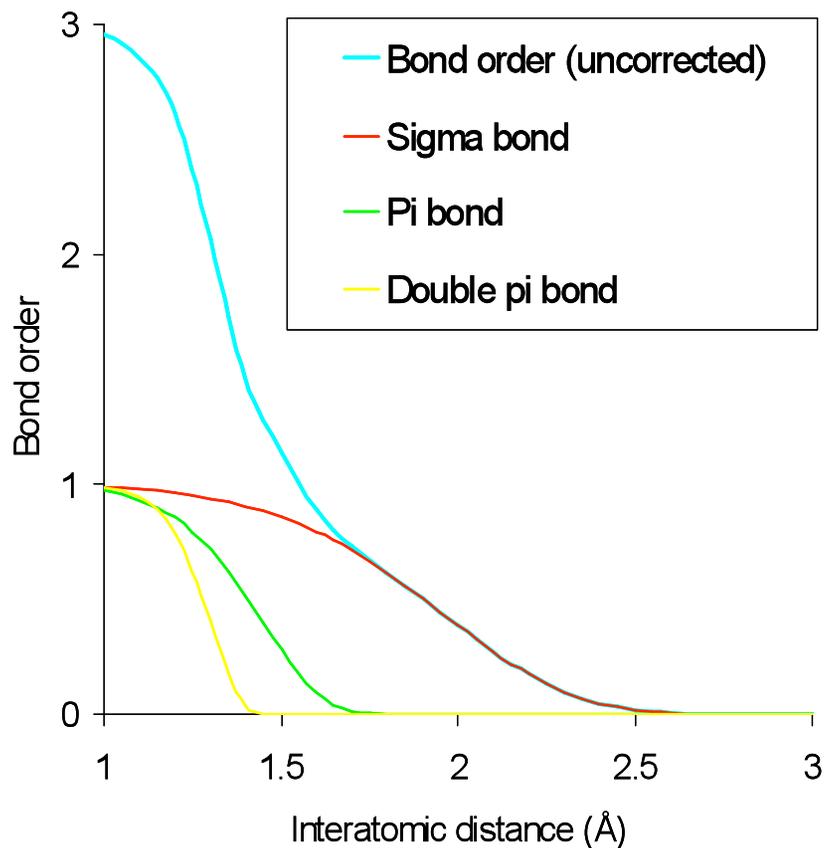
- ReaxFF uses a geometry-dependent charge calculation scheme [5] that accounts for polarization effects.

1. Abell, G. C., (1985) Phys. Rev. B 31.
2. Brenner, D. W., (1990) Phys. Rev. B **42**, 9458-9471
3. Tersoff, J., (1988) Phys. Rev. Lett. **61**, 2879-2882.
4. van Duin, A. C. T., Dasgupta, S., Lorant, F., and Goddard, W. A., (2001) J. Phys. Chem. A **105**, 9396-9409.
5. Mortier, W. J., Ghosh, S. K., and Shankar, S. (1986) JACS **108**, 4315-4320.

Introduction of bond orders

Calculation of bond orders from interatomic distances

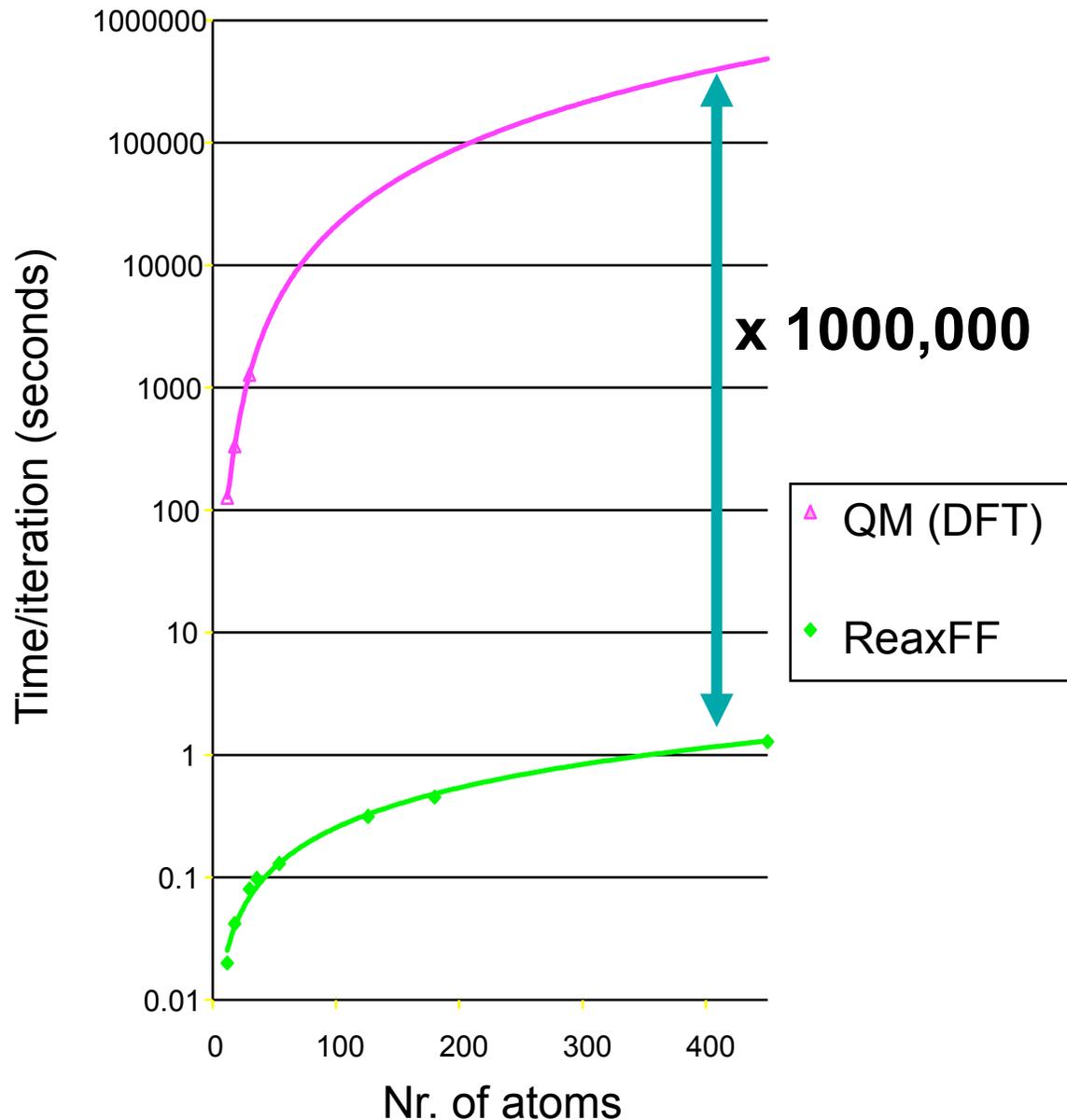
$$BO_{ij} = \exp \left[p_{bo,1} \cdot \left(\frac{r_{ij}}{r_o^\sigma} \right)^{p_{bo,2}} \right] + \exp \left[p_{bo,3} \cdot \left(\frac{r_{ij}}{r_o^\pi} \right)^{p_{bo,4}} \right] + \exp \left[p_{bo,5} \cdot \left(\frac{r_{ij}}{r_o^{\pi\pi}} \right)^{p_{bo,6}} \right]$$



General rules for ReaxFF

- MD-force field; no discontinuities in energy or forces even during reactions.
- User should not have to pre-define reactive sites or reaction pathways; potential functions should be able to automatically handle coordination changes associated with reactions.
- Each element is represented by only 1 atom type in the force field; force field should be able to determine equilibrium bond lengths, valence angles etc. from chemical environment.

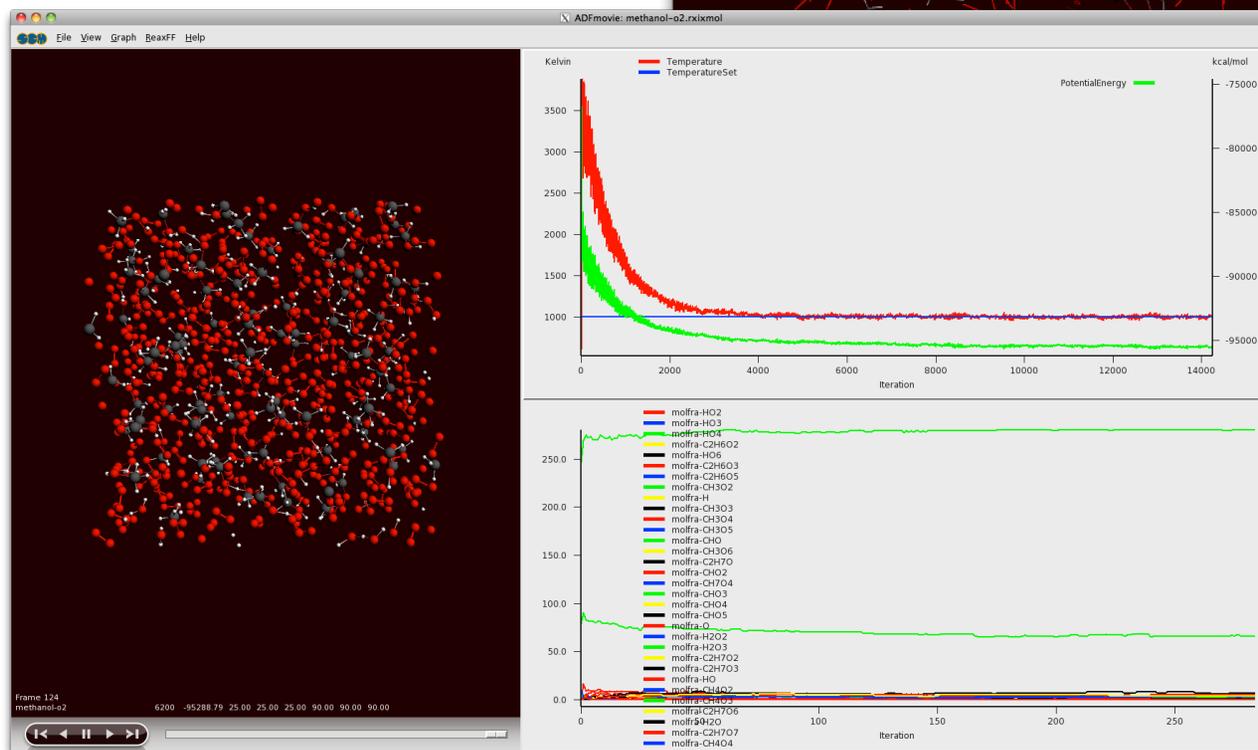
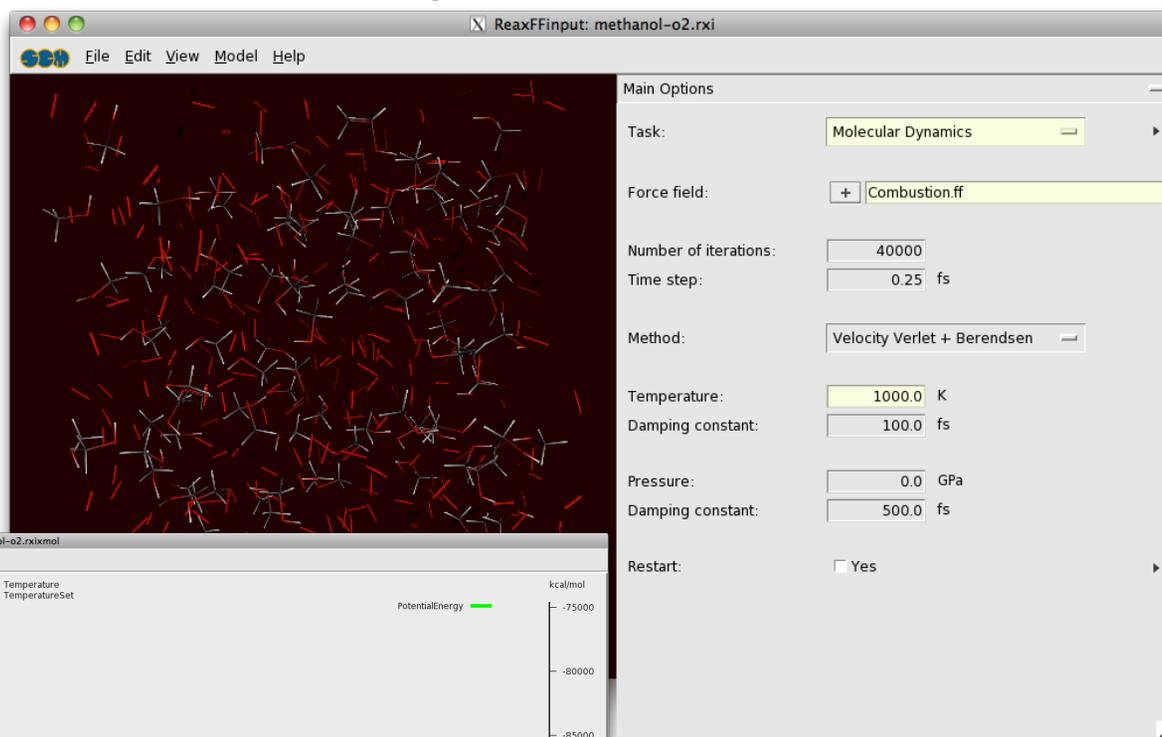
ReaxFF Computational expense



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

ReaxFF integration into ADF/BAND graphical user interface

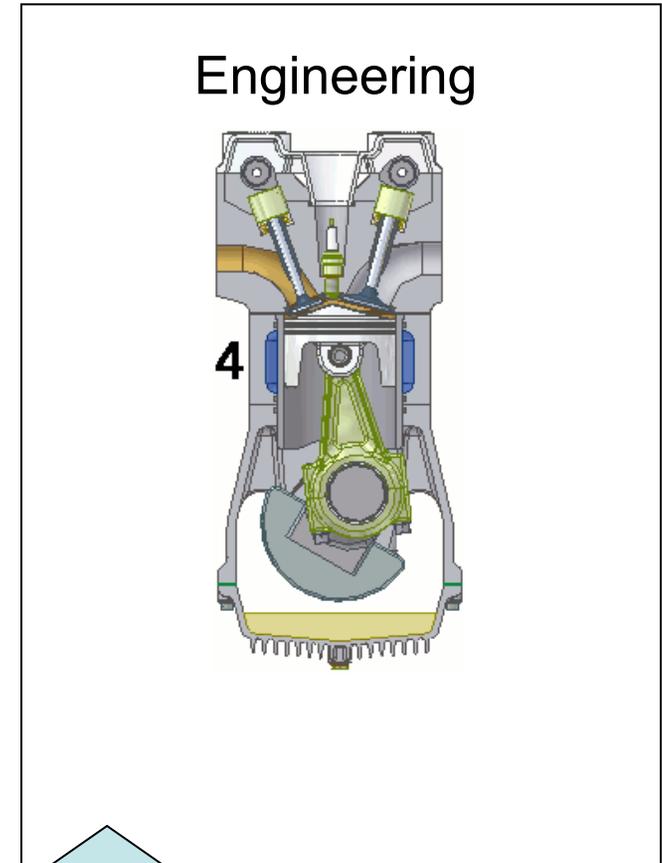
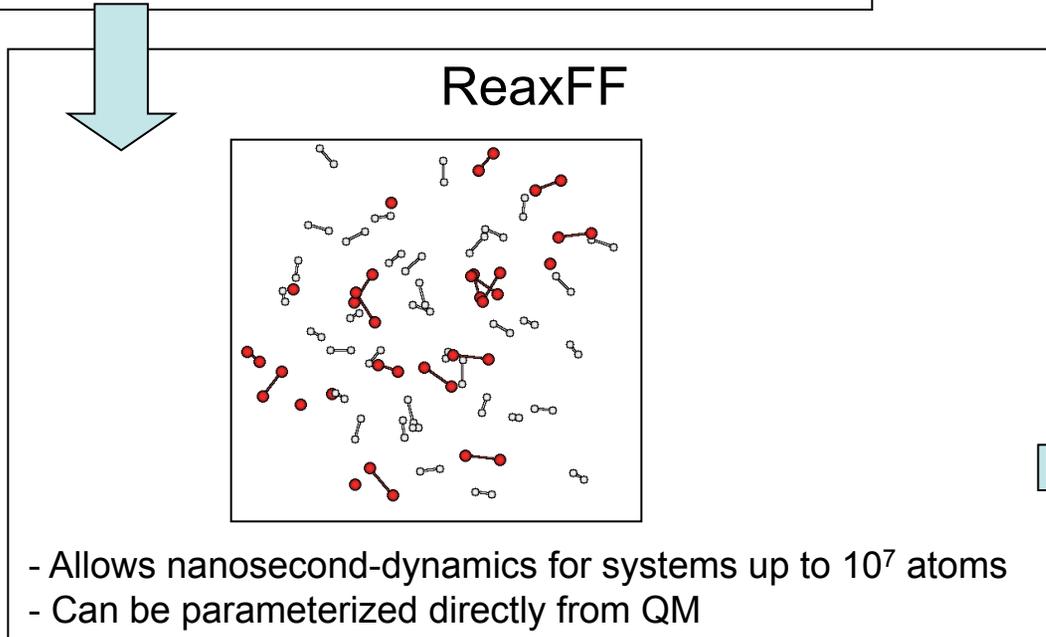
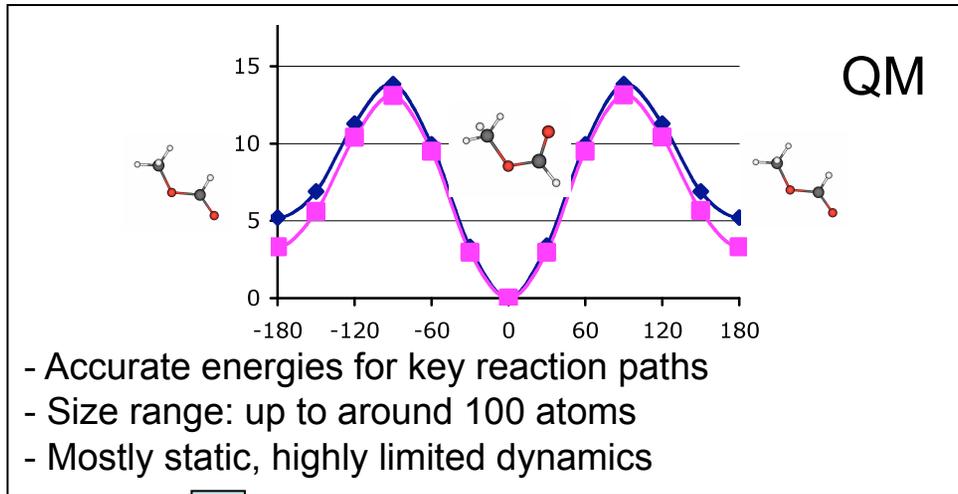
- Collaboration with SCM.
- Professional software support team.
- Beta-version GUI available
- Parallel version + code optimization planned.
- Direct integration of state-of-the-art DFT/FF/TB codes.



Integration team:

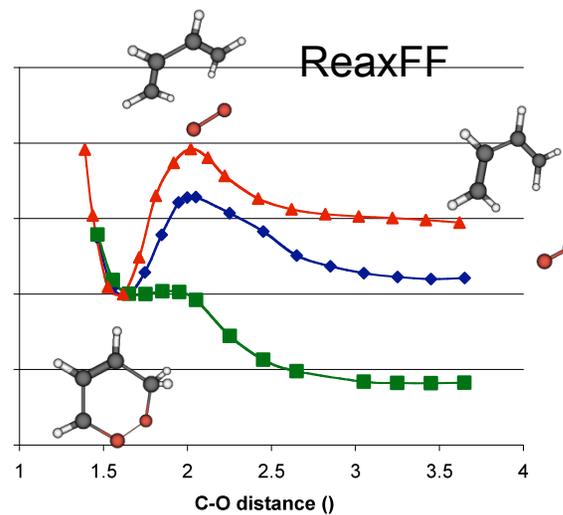
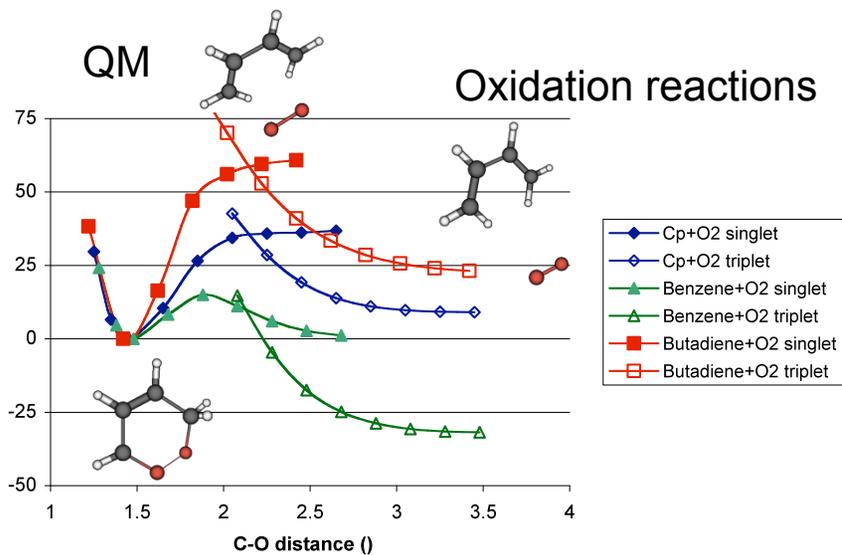
- Stan van Gisbergen, Olivier Visser, Alexei Yakovlev (SCM)
- Mike Russo, Kaushik Joshi (Penn State)

Combustion reactions



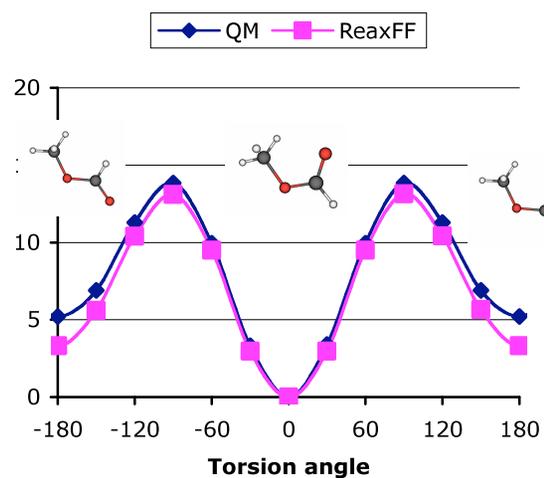
Database of reaction kinetics and diffusion constants

Force field development: hydrocarbon oxidation

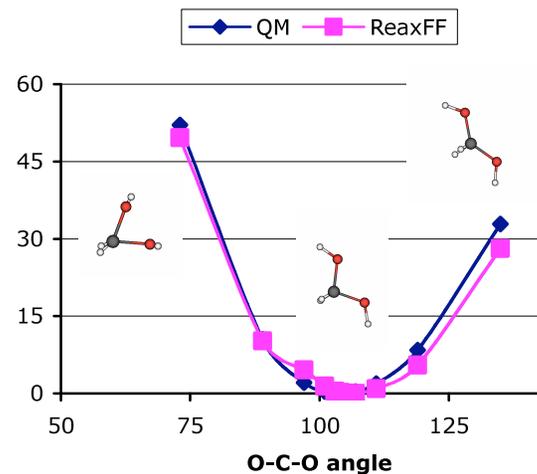


QM: Jaguar/DFT/B3LYP/6-311G**

Rotational barriers

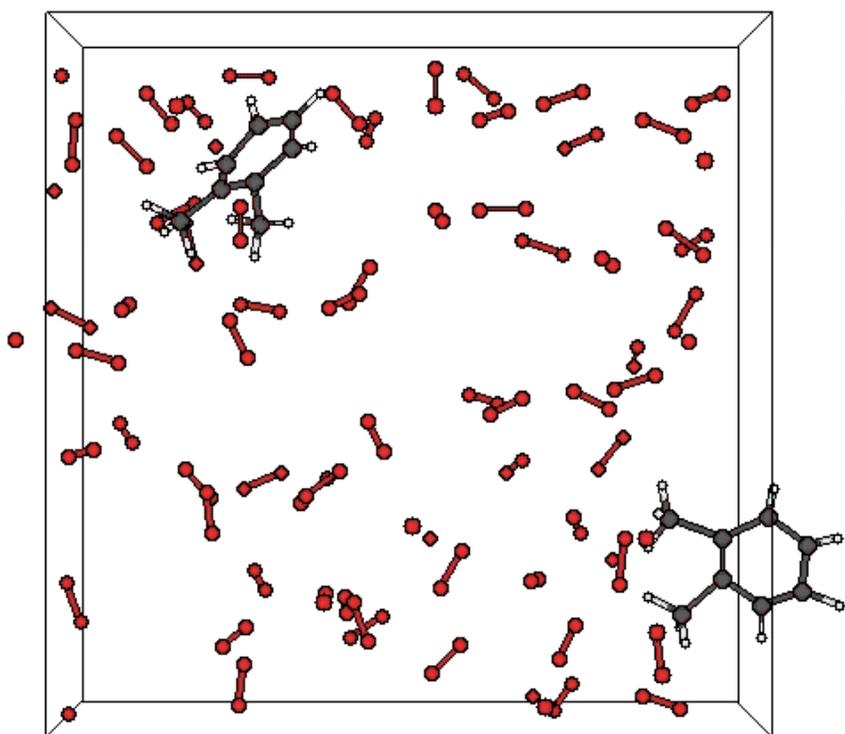


Angle strain

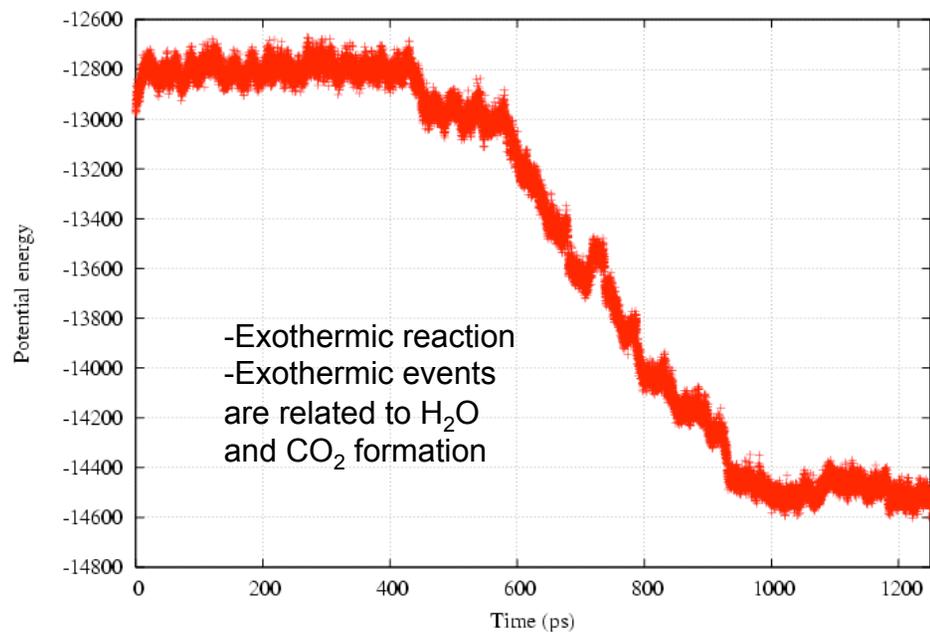
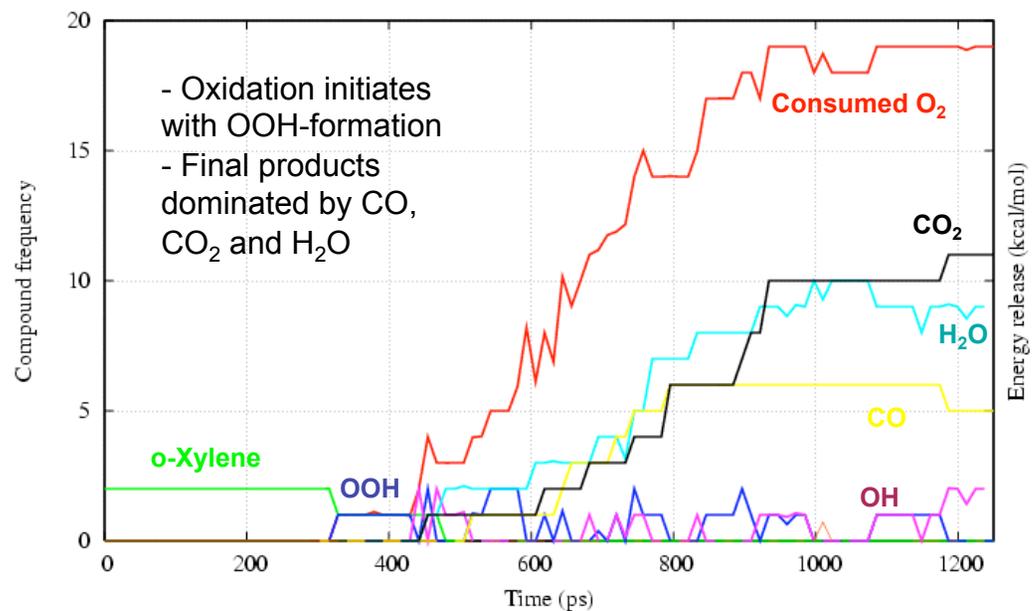


- total training set contains about 1700 compounds

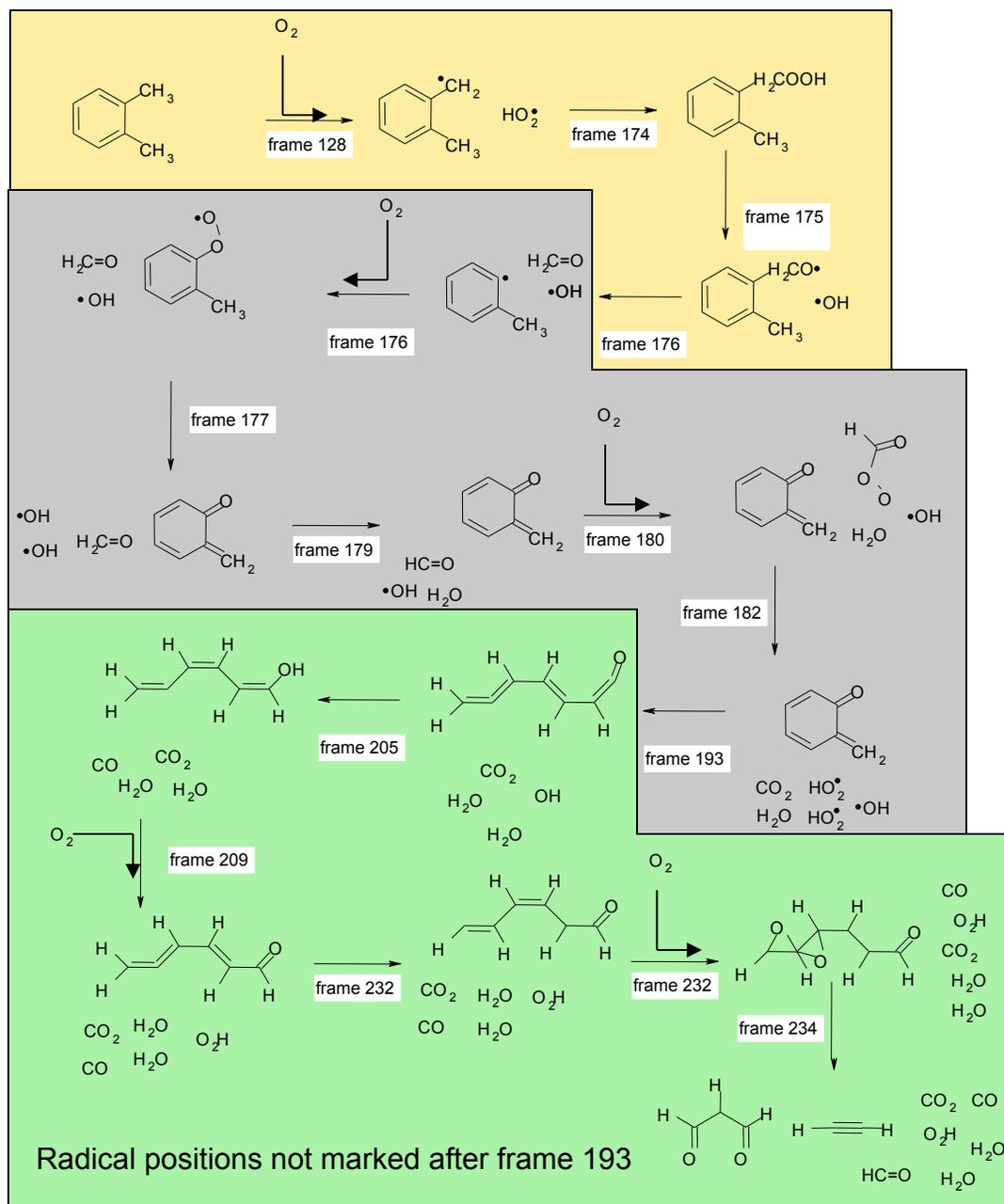
Test ReaxFF CHO-description: oxidation of o-xylene



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



o-Xylene oxidation: Detailed reaction mechanism



- Reaction initiation with HO_2^\bullet formation

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

- Only after $\text{H}_2\text{C}=\text{O}$ is formed and dissociated the benzene ring gets oxidized

- Ring opens shortly after destruction of aromatic system

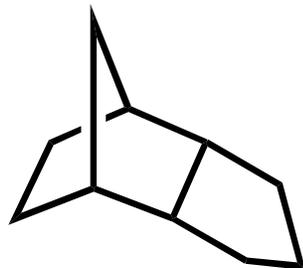
- Ring-opened structure reacts quickly with oxygen, forming CO_2 , H_2O and CO

-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)

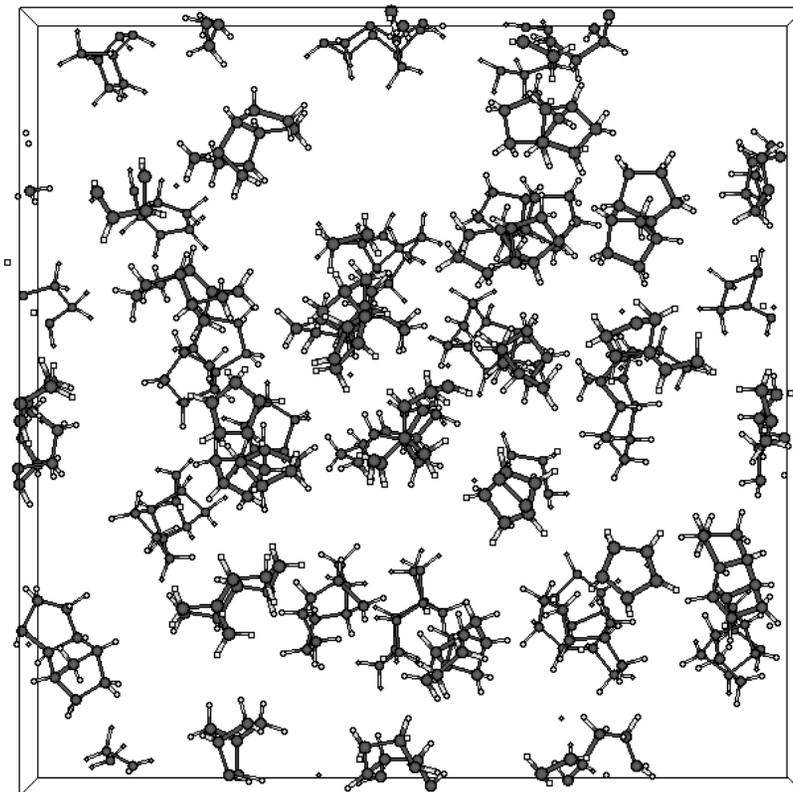


Exo-tetrahydrodicyclopentadiene: JP-10

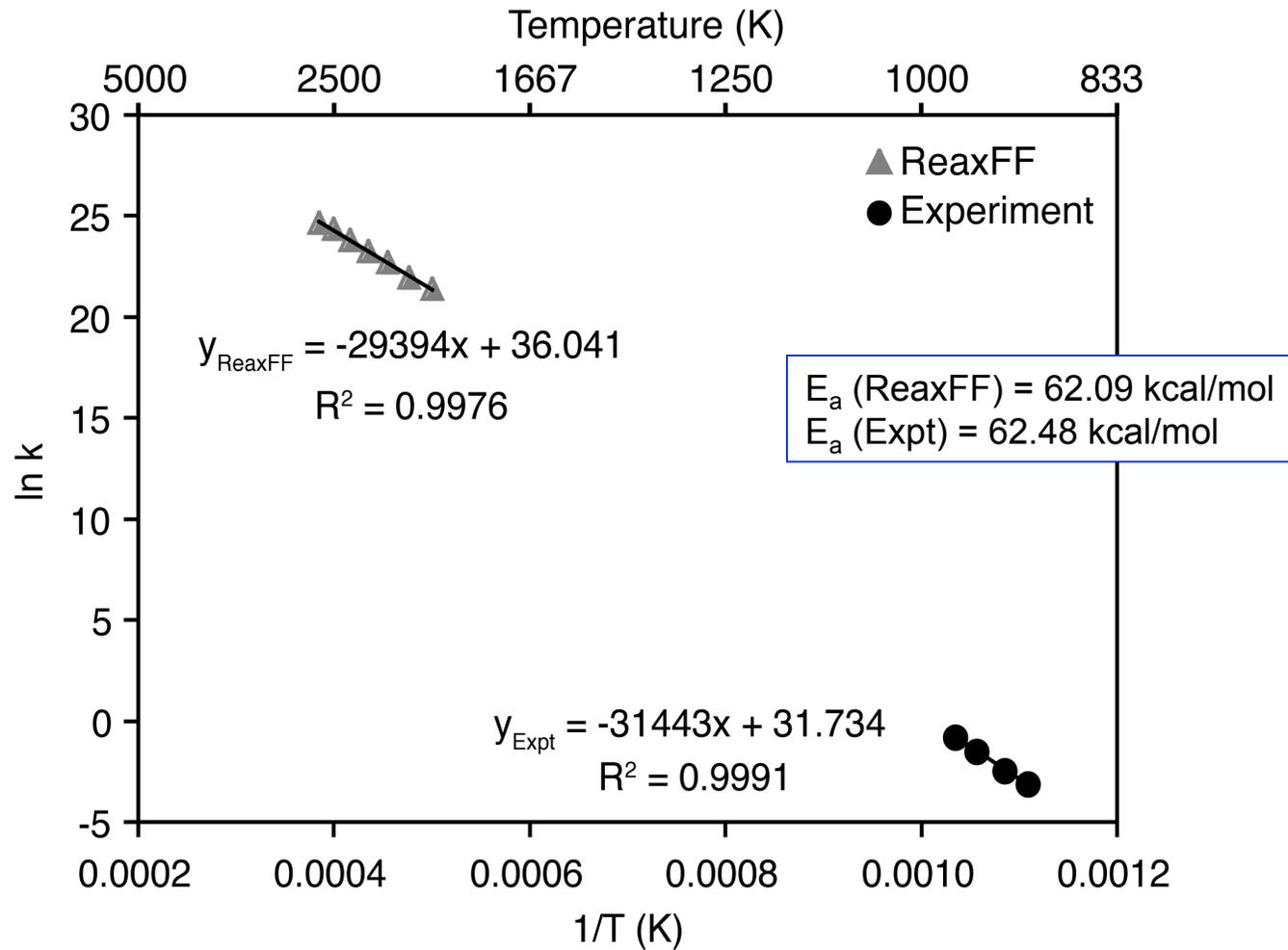
- **Synthetic high-energy density fuel**
 - Volumetric heat content: 39434 MJ/m³ (141500 BTU/gal); high strain leads to high energy output
 - Potential use in pulse detonation engines and missile applications
 - Single component fuel
- **Mechanism is incomplete**
 - No clean mechanism for either pyrolysis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

Simulation strategy for JP-10 pyrolysis

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



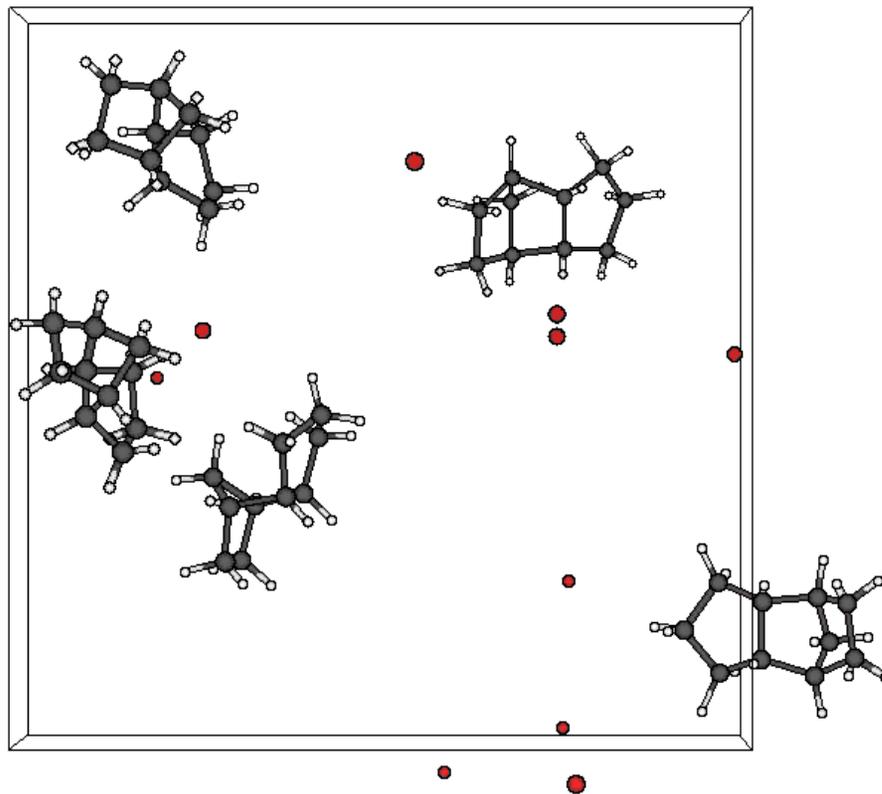
Kinetics for JP-10 Pyrolysis



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

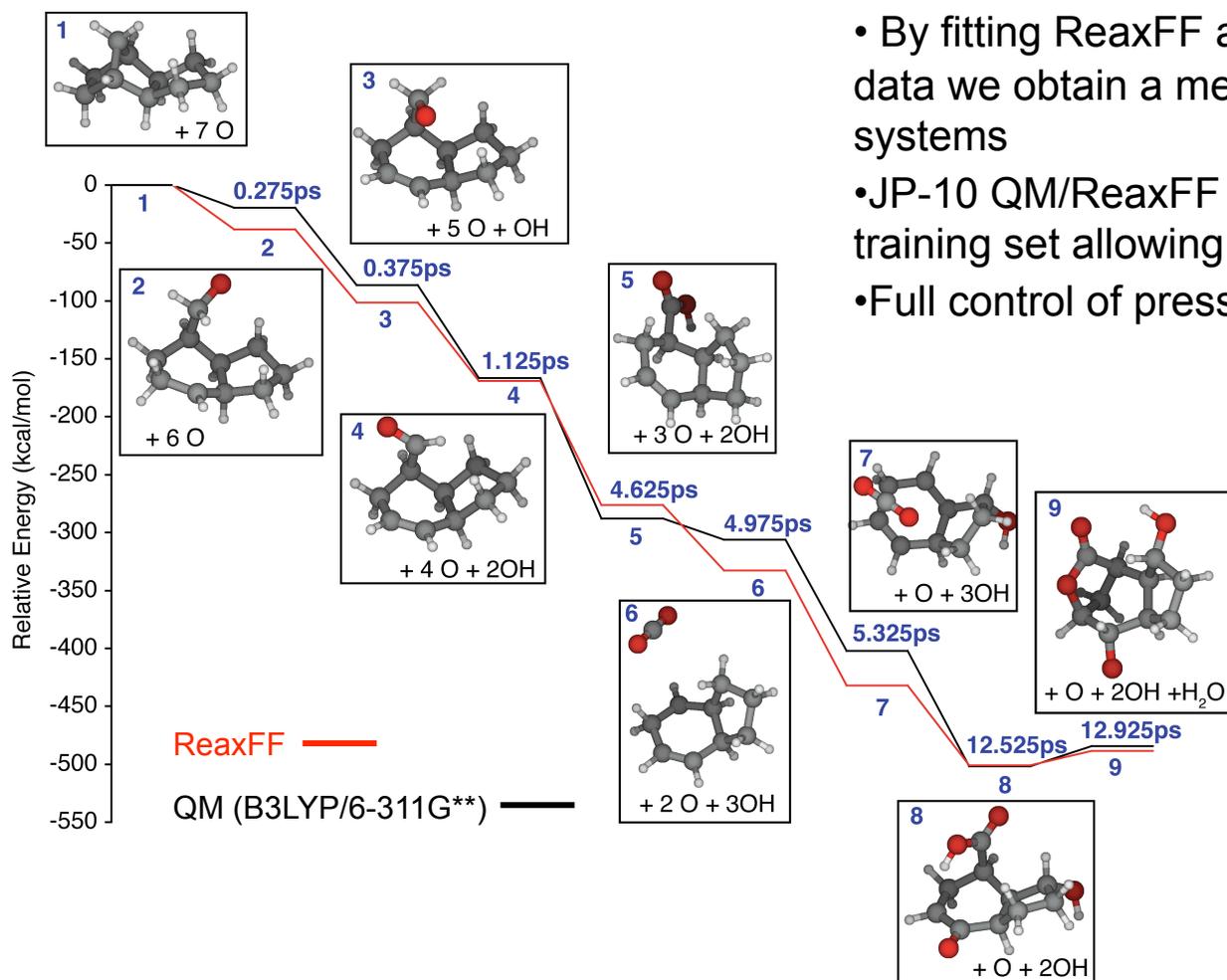
Simulation strategy for JP-10 oxidation

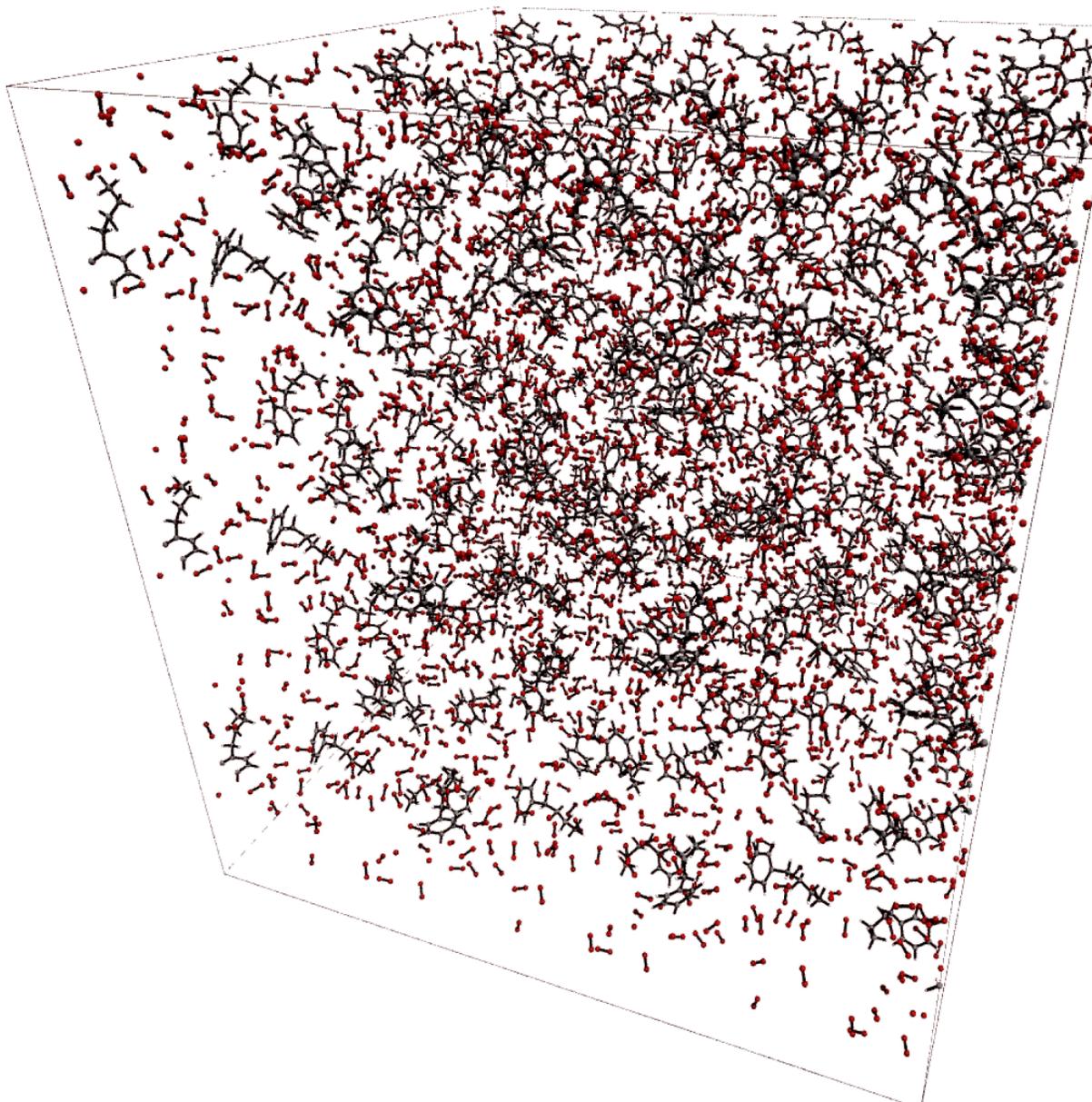
- **5 JP-10 molecules**
- **10 oxygen radicals**
- 140 atoms
- Density = 0.174 g/cm^3
- Equilibrated at 1000K for 5 ps
- Temperature control using Berendsen thermostat with 0.1 ps damping constant
- MD time step of 0.1 fs
- **Total simulation time: 10 ps**
- **Performed a NVT-MD simulation at 1000K**
- **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

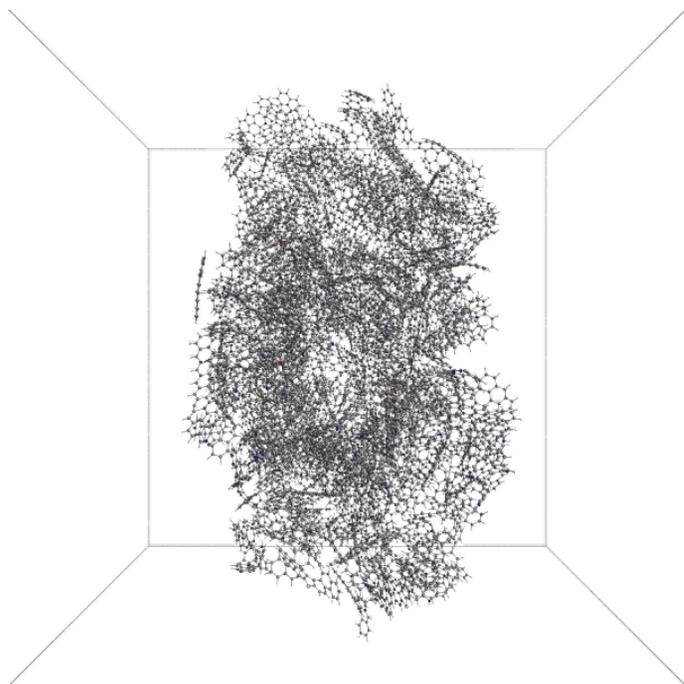




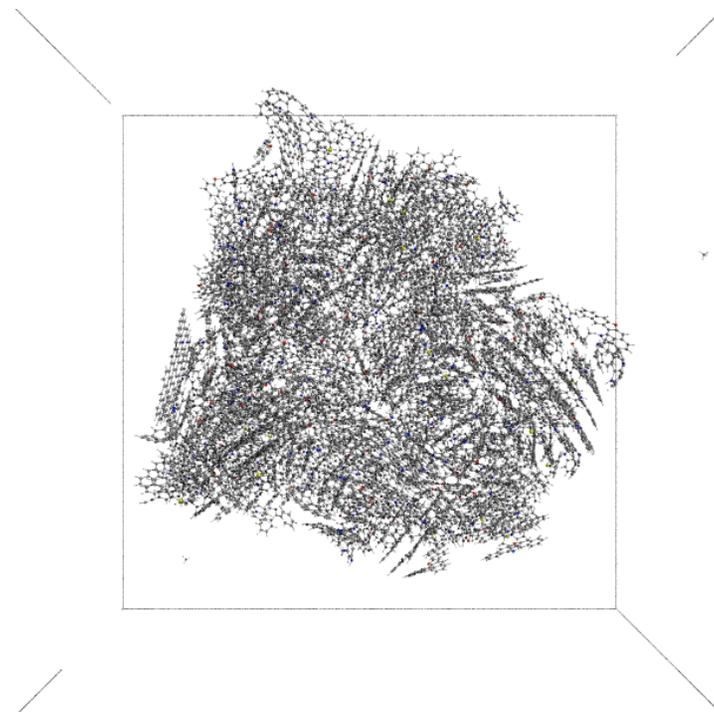
Simulation by Mike Russo,
Penn State

LAMMPS/ReaxFF Parallel MD-simulation on hydrocarbon combustion
T=2500K, n=12,000 atoms, 4 processors; CPU-time: 4 hours

Initial application to coal pyrolysis (ADF/ReaxFF)



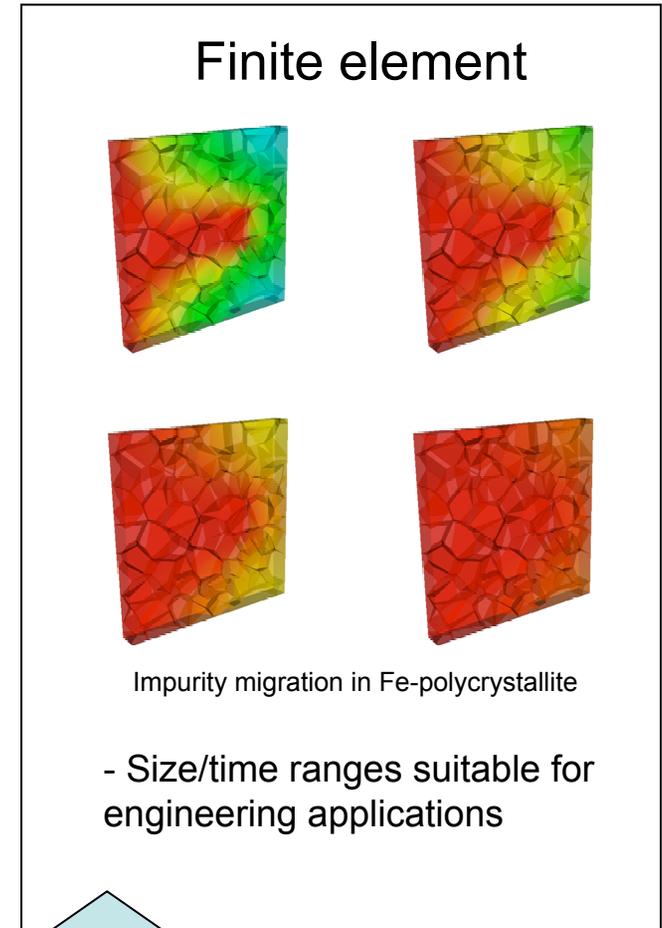
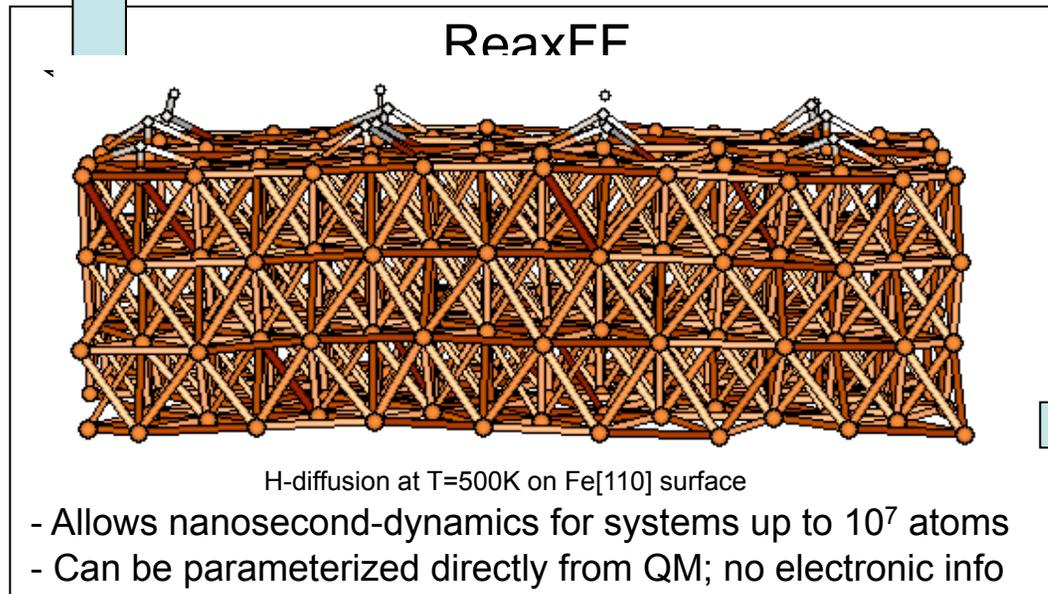
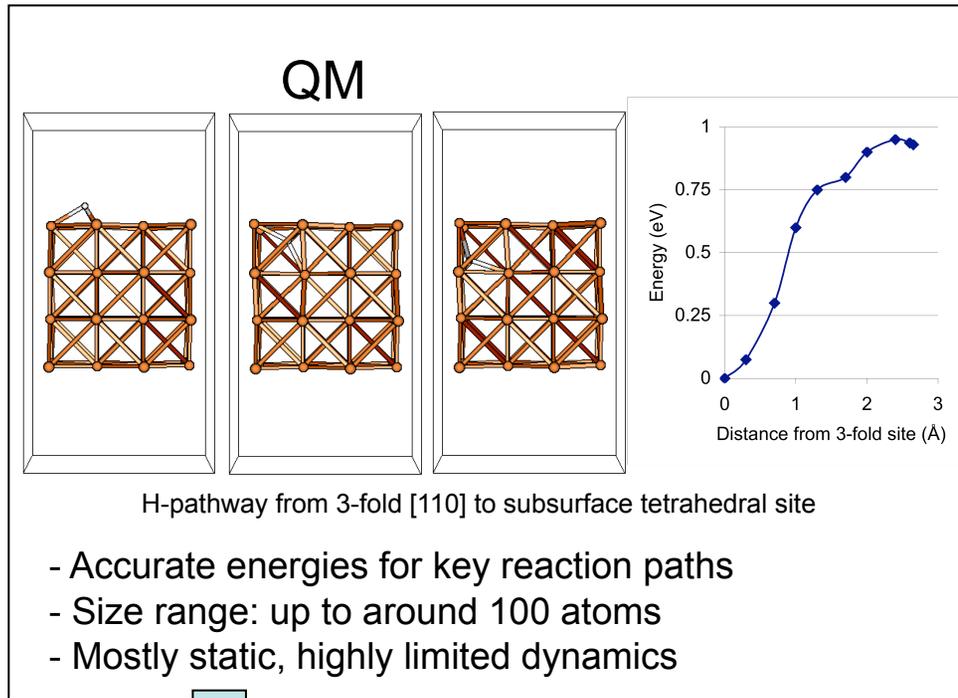
Coal structure, 20,000 atoms
C:S ratio: 100:1, from Fringe3D [1]



MD simulation with
temperature ramp

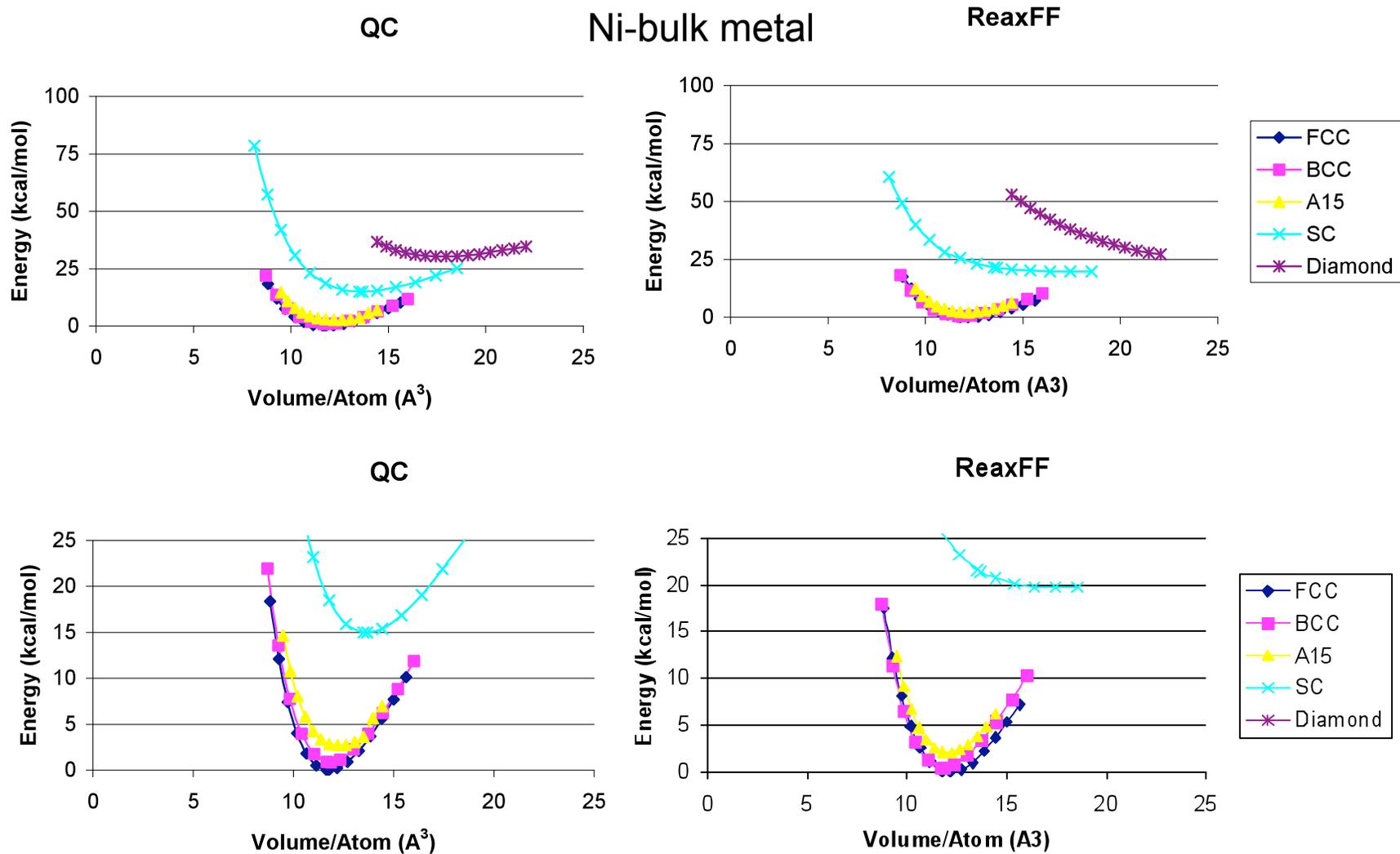
[1] Fernandez-Alos, V., J.K. Watson, and J.P. Mathews. *Directly capturing aromatic structural features in coal via "Fringe3D" generating 3D molecular models directly from HRTEM lattice fringe images.* in *Prepr. Pap.-Am. Chem. Soc., Div. Fuel Chem.* 2009. Salt Lake City, UT.

Material failure



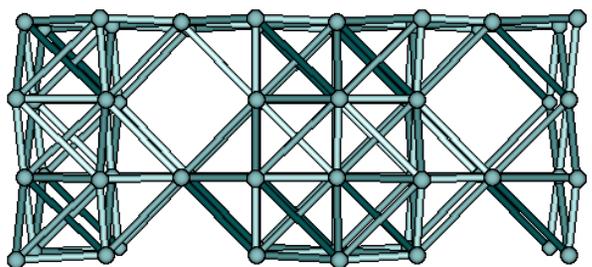
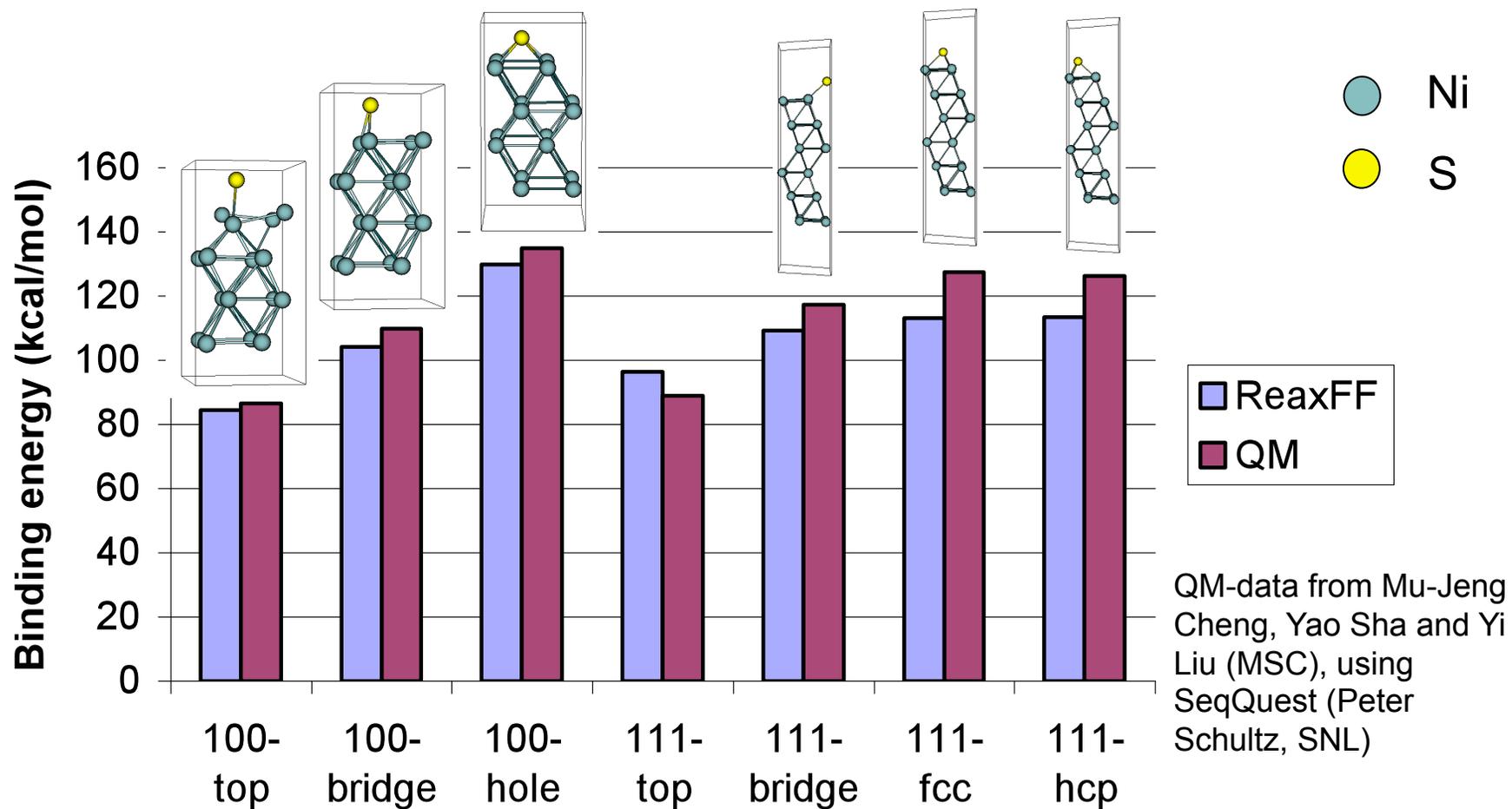
Database of temperature, pressure and concentration dependent diffusion/ decohesion rules

Development of a ReaxFF potential for Ni/S systems

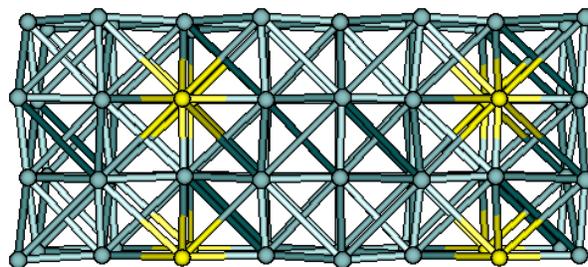


- Other data in training set: cohesive energy, surface energy (111 and 100), vacancy formation energy

Sulfur binding energies to Ni-surface and subsurface sites



Ni₇Vac₁



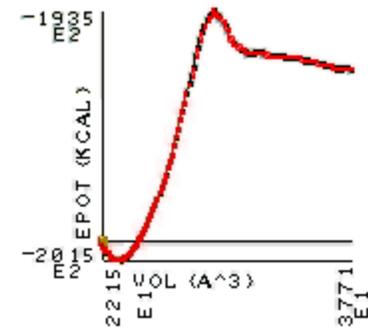
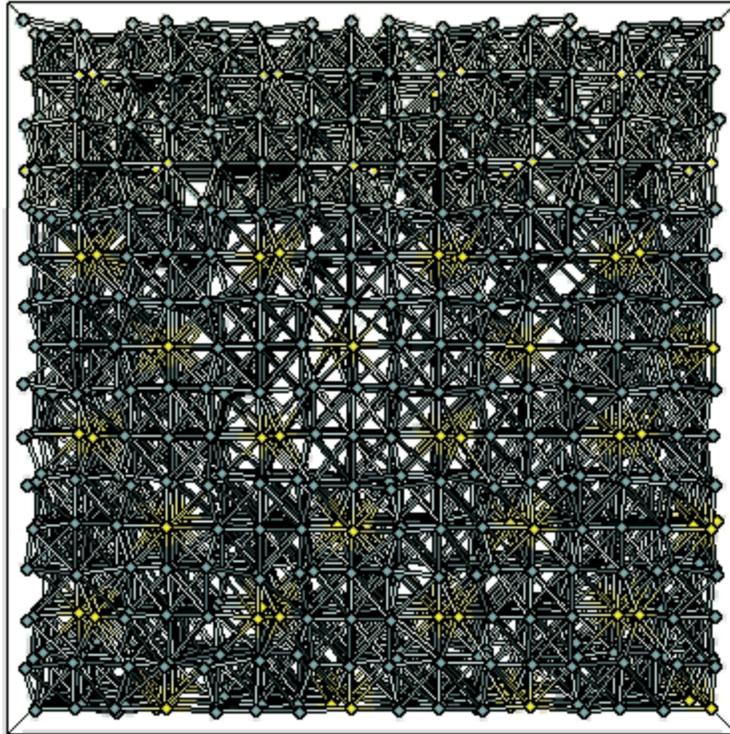
Ni₇S₁

$$\Delta E_{\text{QM}} = 95.0 \text{ kcal/molS}$$

$$\Delta E_{\text{Reax}} = 94.9 \text{ kcal/molS}$$

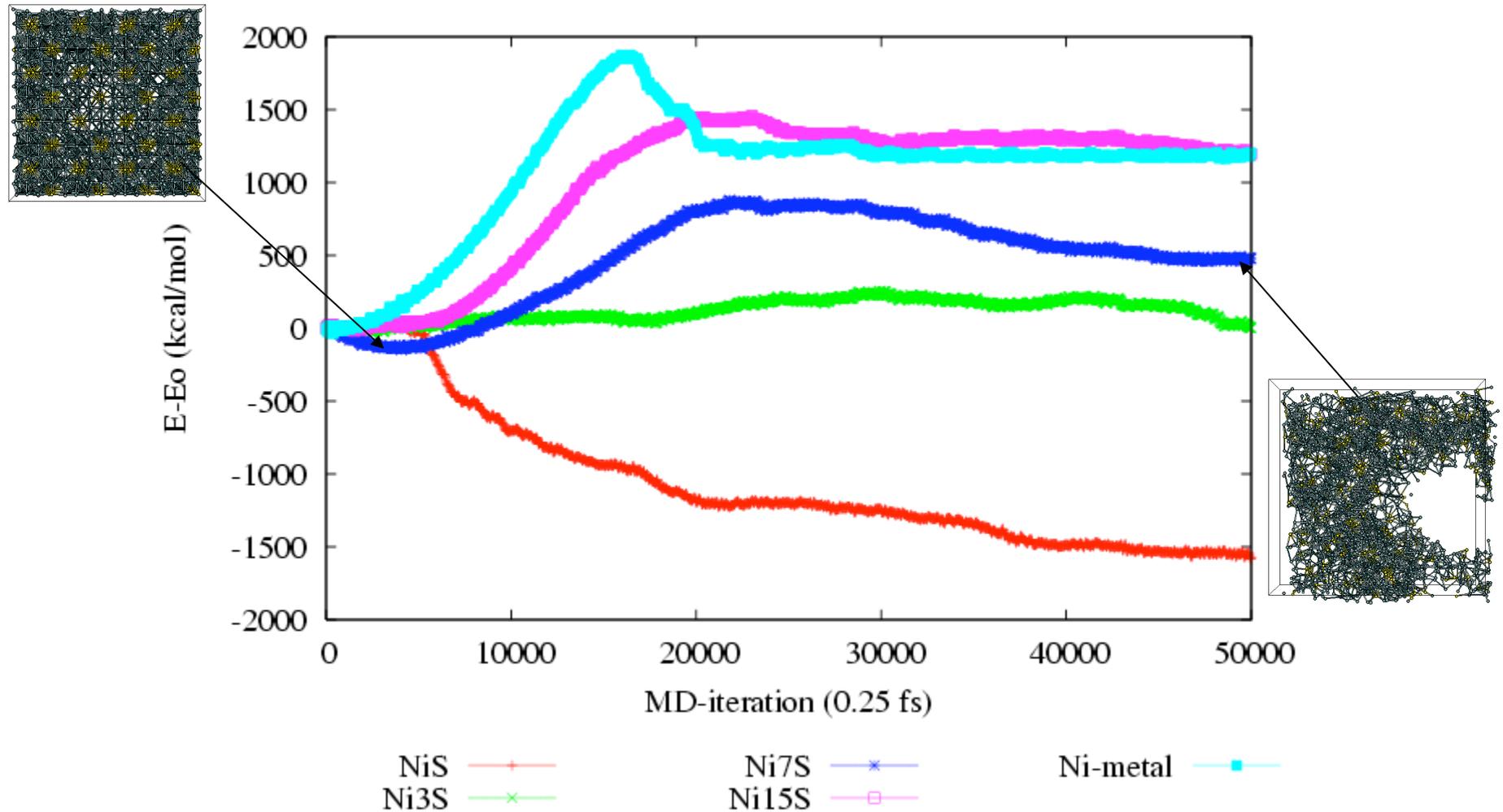
- Sulfur strongly prefers surface-sites

Simulations on material failure as a function of S-concentration



- Ni₇S-phase; expansion in 111-direction
- 2048 atoms; T=300K; NVT-simulation

Simulations on material failure as a function of S-concentration

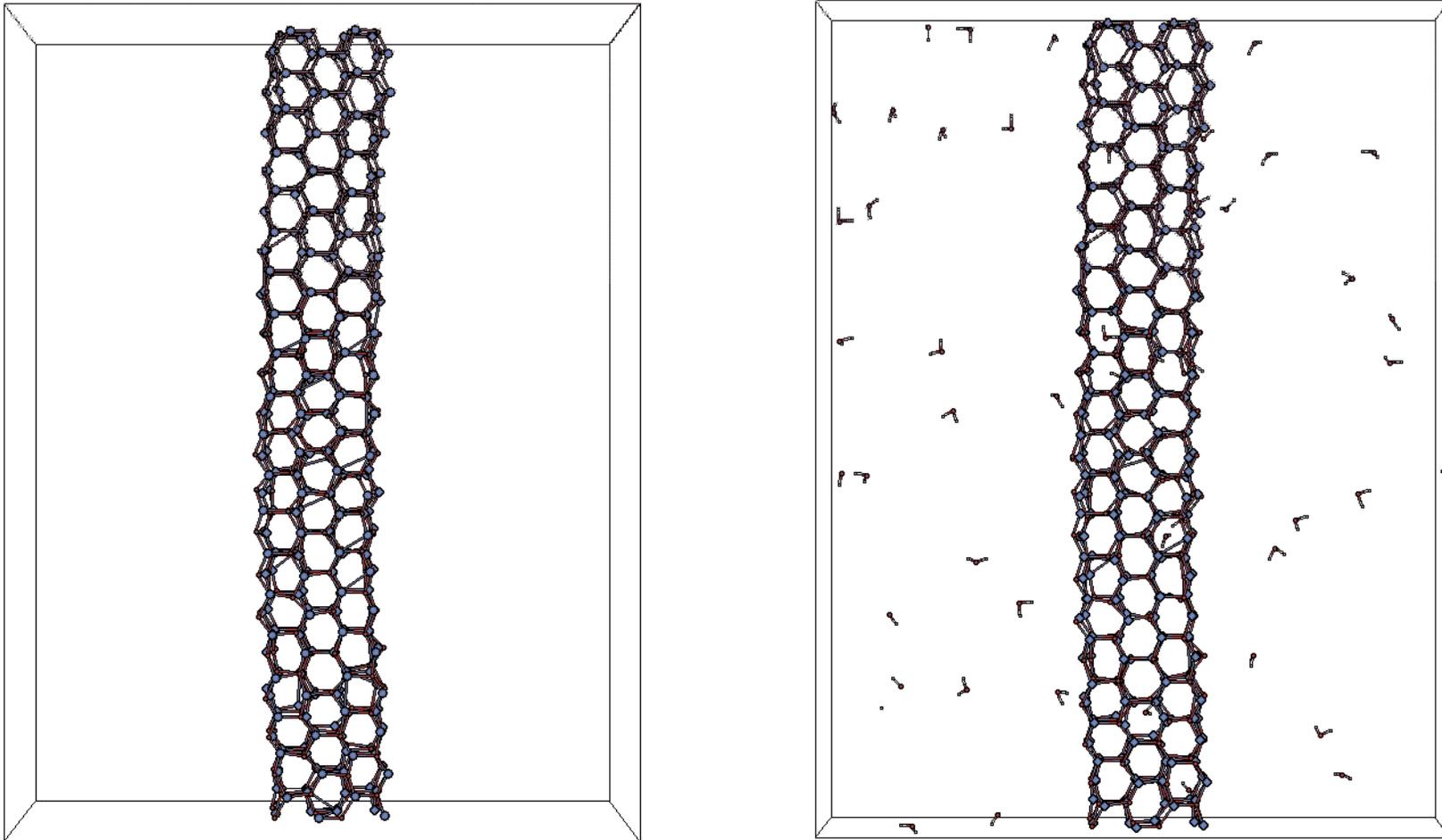


- Sulfur significantly weakens the material
- Surface formation becomes exothermic at high sulfur concentrations

Chen, Kalla, Kaxiras, Lu, Nakano, Nomura, van Duin, Vashista and Yuan, PRL (2010)

Simulation of ZnO nanowire response to local heating

With Mike Russo and Arvind Bharati



Central region: temperature pulse of 2500K

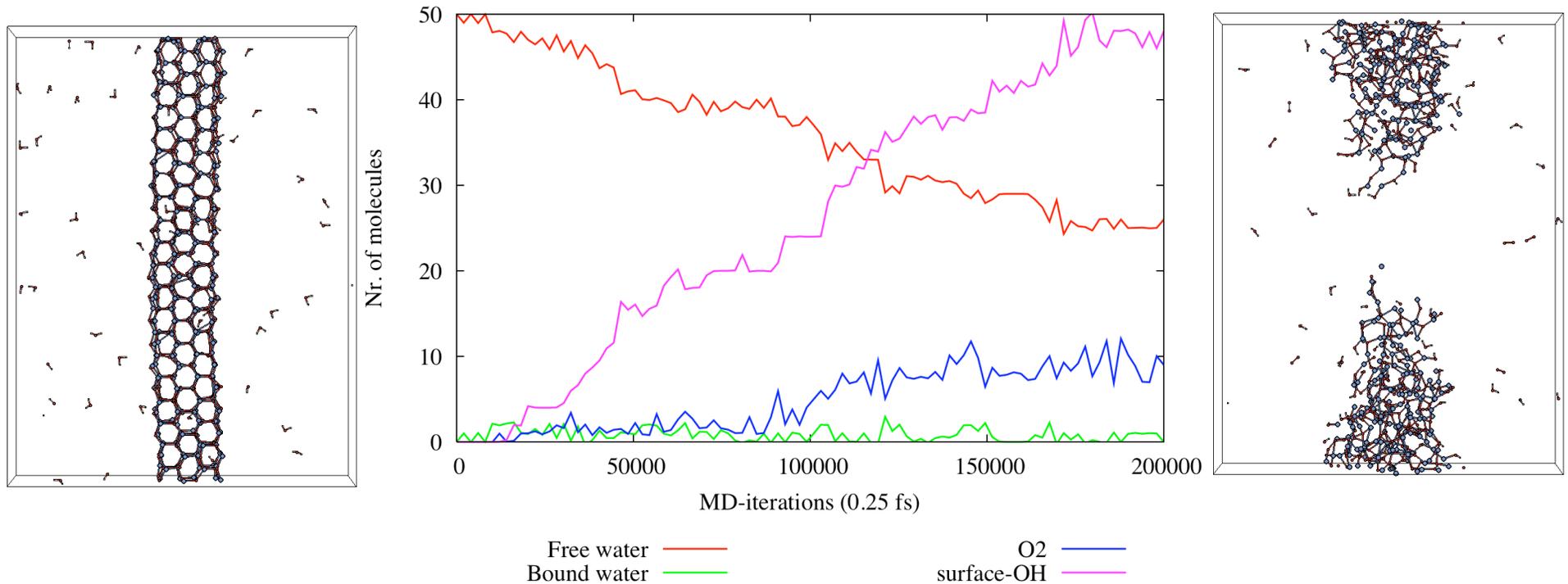
Rest of the structure: NVE-dynamics

Collaboration with David Raymand and Kersti Hermannsson (Uppsala)

[1] Raymand, van Duin, Baudin and Hermannsson, Surface Science 2008

[2] Raymand, van Duin, Spangberg, Hermannsson and Goddard, Surface Science 2010

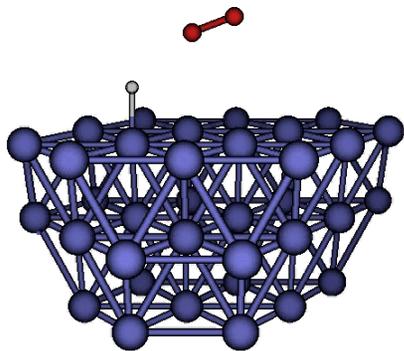
Analysis of ZnO nanowire surface chemistry



- Rapid adsorption, followed by dissociation, of water molecules
- Dissociated water assists in the breakup of the nanowire
- Release of O₂ 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

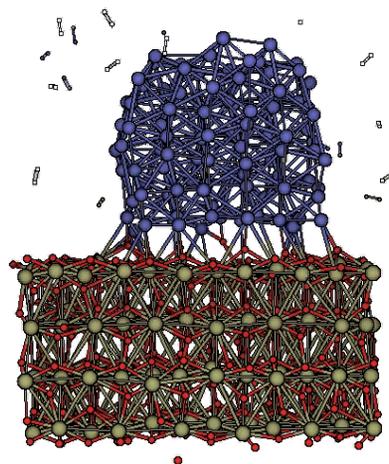
Catalysis

QM



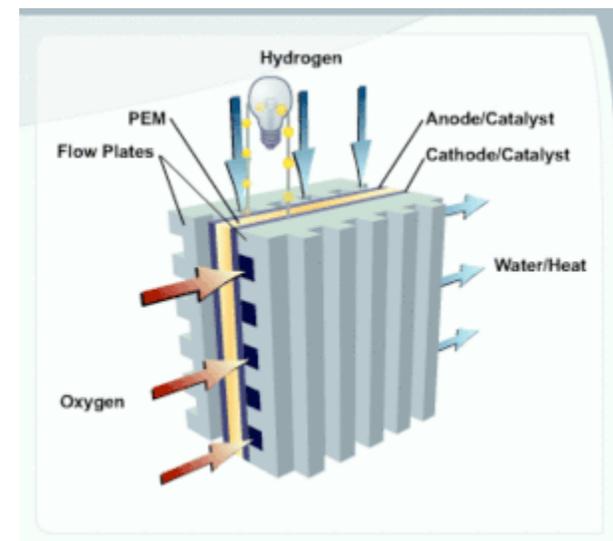
- Accurate energies for key reaction paths
- Size range: up to around 100 atoms

ReaxFF



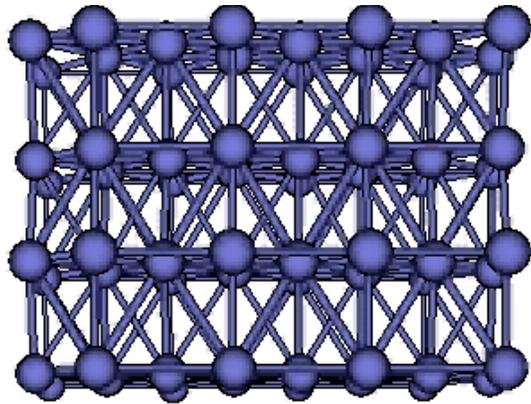
- Allows nanosecond-dynamics on multi-component systems
- Can be parameterized directly from QM

Engineering

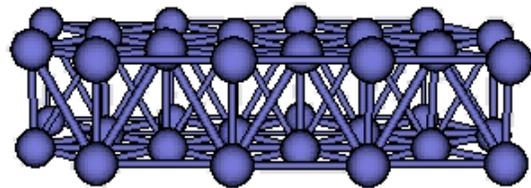
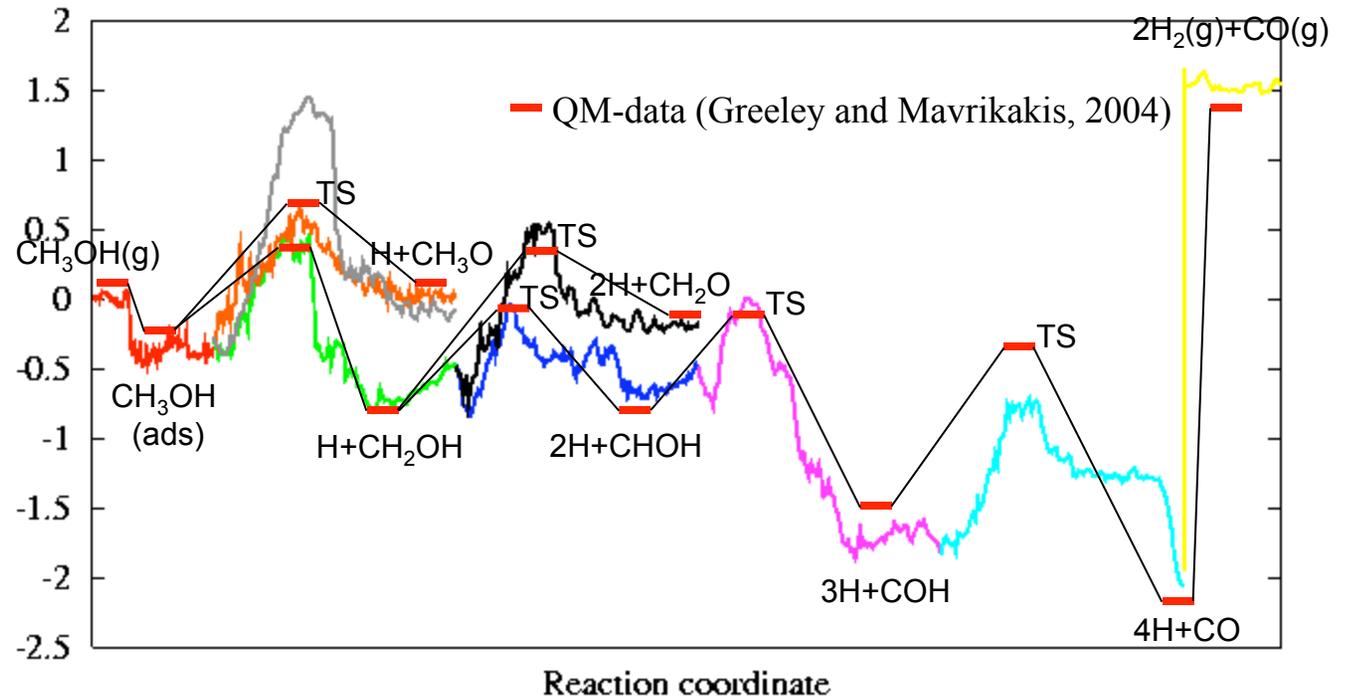


- Interface properties
- Reaction kinetics
- Diffusion constants

QM/ReaxFF methanol reaction pathways



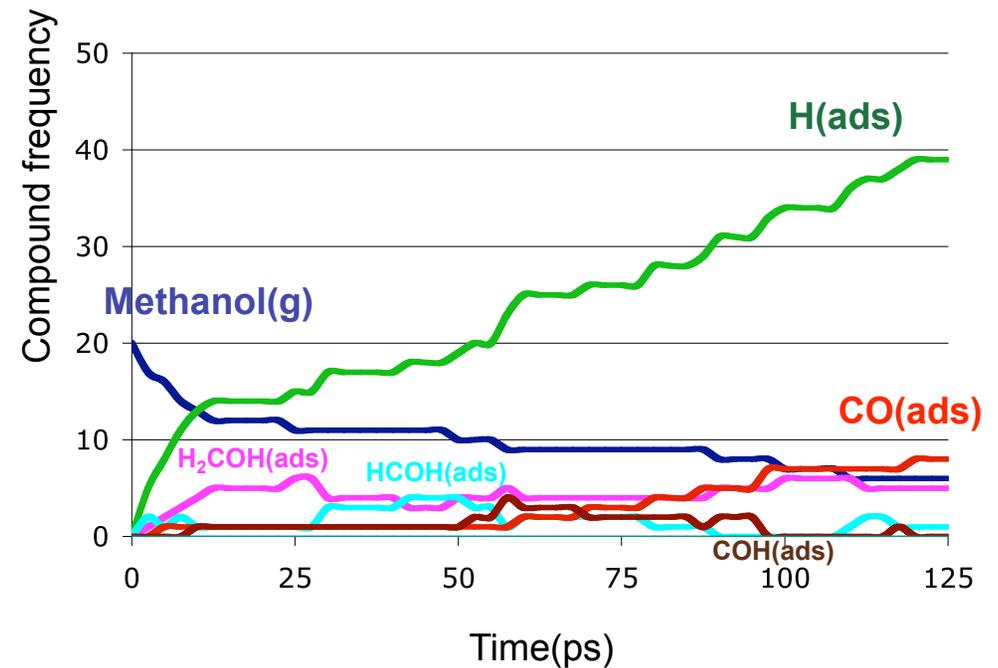
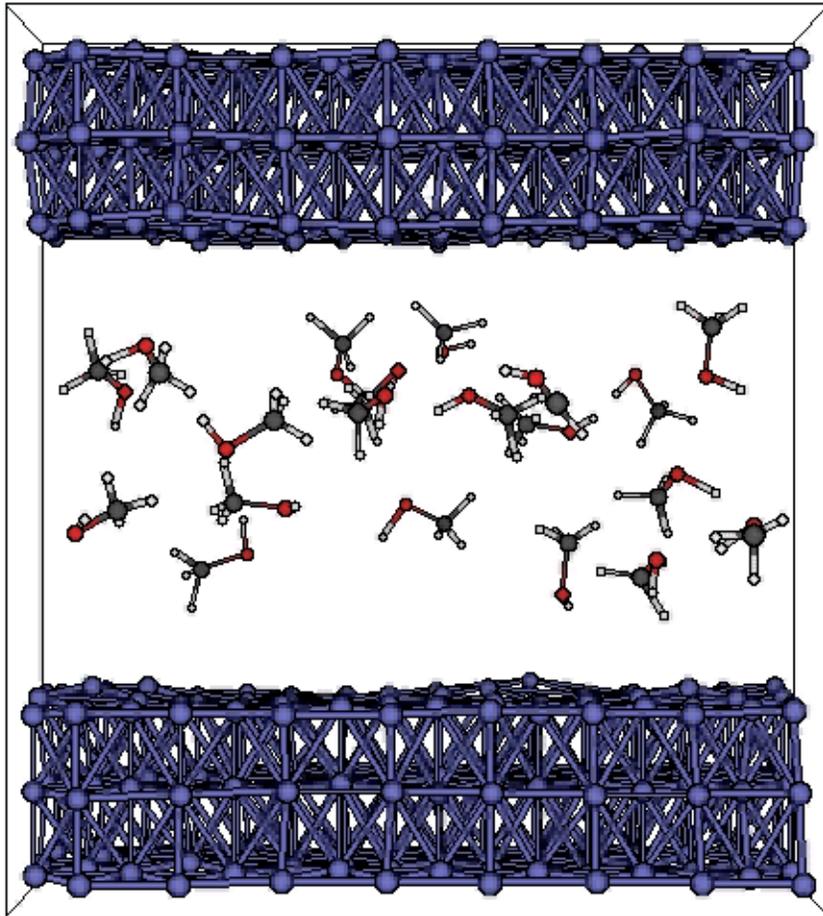
Methanol reaction on Pt[111] surface



- Excellent agreement between ReaxFF and QM for entire reaction path

Methanol conversion on Pt[111]-surface

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



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

Summary

- ReaxFF has proven to be transferable to a wide range of materials and can handle both complex chemistry and chemical diversity. Specifically, ReaxFF can describe covalent, metallic and ionic materials and interactions between these material types.
- The low computational cost of ReaxFF (compared to QM) makes the method suitable for simulating reaction dynamics for large (>> 1000 atoms) systems (single processor). ReaxFF has now been parallelized, allowing reactive simulations on >>1000,000 atoms.

| period | group | | | | | | | | | | 13 | 14 | 15 | 16 | 17 | 18 | | |
|--------|-------|-----|--------|-----|-----|-----|------|-------|-------|-----|------|-----|----|-----|------|-------|----|----|
| | 1* | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 | IIIb | IVb | Vb | VIb | VIIb | VIIIb | | |
| | Ia | IIa | IIIa** | IVa | Va | VIa | VIIa | VIIIa | VIIIa | X | IIIa | IVa | Va | VIa | VIIa | 0 | | |
| 1 | H | | | | | | | | | | | | | | | He | | |
| 2 | Li | Be | | | | | | | | | | | | | | Ne | | |
| 3 | Na | Mg | | | | | | | | | | | | | | Ar | | |
| 4 | K | Ca | Sc | Ti | V | Cr | Mn | Fe | Co | Ni | Cu | Zn | Ga | Ge | As | Se | Br | Kr |
| 5 | Rb | Sr | Y | Zr | Nb | Mo | Tc | Ru | Rh | Pd | Ag | Cd | In | Sn | Sb | Te | I | Xe |
| 6 | Cs | Ba | La | Hf | Ta | W | Re | Os | Ir | Pt | Au | Hg | Tl | Pb | Bi | Po | At | Rn |
| 7 | Fr | Ra | Ac | 104 | 105 | 106 | 107 | 108 | 109 | 110 | 111 | 112 | | | | | | |

 : not currently described by ReaxFF

Acknowledgements / Contact information

- Collaborators:
- Satyam Agrawalla, Amar Kamat and Mike Russo (Penn State)
 - Jonathan Mathews, Jim Kubicki, Mike Janik (Penn State)
 - David Raymand, Kersti Hermansson (Uppsala)
 - Kimberley Chenoweth, Vyacheslav Bryantsev, Bill Goddard (Caltech)
 - Obaidue Rahaman (Ramie) and Doug Doren (U. Delaware)

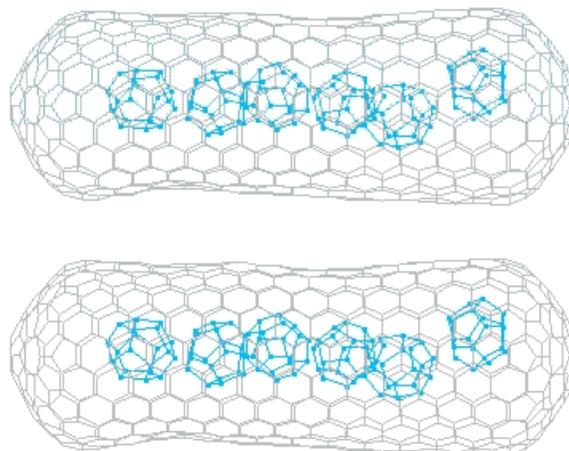
- Funding:
- PSU/KISK startup grant
 - Illinois Coal
 - GM and Exxon (ADF integration)
 - British Royal Society (initial ReaxFF funding)

Website:

<http://www.engr.psu.edu/adri/>

Phone: 814-863-6277

E-mail: acv13@psu.edu



ReaxFF simulation of the collision between two closed carbon nanotubes filled with highly-reactive N₂₀-molecules. Impact velocity: 4 km/sec

