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

Adri van Duin, Mike Russo, Kaushik Joshi and Amar Kamat

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

Pyrolysis of a sulphurized hydrocarbon mixture

Noble gas accommodation coefficients on a graphene wafer

Conversion of formaldehyde on a iron particle

Purdue June 2011
Engineering challenges....

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

Coal power plant

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

Fuel cell

...require atomistic-scale solutions

Pre-oxidized Al-tube with ethylene/O\textsubscript{2}/ozone mixture

Ni-particle reacting with propene at T=1500K
Solving the size/time gap between simulation and experiment

- Atomistic simulations
- ReaxFF
- QM

- Time
- Distance
- Hours

- Improving experimental resolution
- Increasing computer speed

- 10^{-15}
- Ångstrom
- Meters
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)
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

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

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

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

- 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.
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].

Calculation of bond orders from interatomic distances

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

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

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

Interatomic distance (Å)

Bond order

- Bond order (uncorrected)
- Sigma bond
- Pi bond
- Double pi bond
ReaxFF energy barriers

ReaxFF barrier for H₂ conversion to H₂S on a MoS₂ catalyst (collaboration with Nadia Sellami and Theo de Bruyn, IFP). DFT data from Prodhomme et al., 2010

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

Comparison of DFT/MD and ReaxFF/MD for 2eV oxygen impact on Si(CH$_3$)$_4$

- ReaxFF reproduces the DFT/MD reaction products and trajectory
- Comparison between DFT/MD and ReaxFF/MD for small systems provides a useful tool for method validation
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 200 research groups
- Over 80 publications in peer-reviewed journals
- Parallel ReaxFF (LAMMPS/ReaxFF) available as open-source
- Integrated in ADF/BAND graphical user interface

ReaxFF transferability

The image shows a periodic table highlighting elements not currently described by ReaxFF.
### ReaxFF user community

<table>
<thead>
<tr>
<th>Name</th>
<th>Institute</th>
<th>Distribution date</th>
<th>Application</th>
</tr>
</thead>
<tbody>
<tr>
<td>Adam Bloch</td>
<td>Vanderbilt U.</td>
<td>June 2009</td>
<td>Silica/water</td>
</tr>
<tr>
<td>Philip Thongpichac (CTP)</td>
<td>Sandia National Lab</td>
<td>July 2005</td>
<td>Incorporations into GRASP</td>
</tr>
<tr>
<td>Albert To</td>
<td>U. Pittsburgh</td>
<td>March 2006</td>
<td>Al₂O₃-phase change</td>
</tr>
<tr>
<td>Alejandro Strachan</td>
<td>Purdue U.</td>
<td>August 2006</td>
<td>Ferrocenean, Si-nanowires</td>
</tr>
<tr>
<td>Alexey Kalekin</td>
<td>Emory University</td>
<td>June 2010</td>
<td>PO₃⁺/PFF development</td>
</tr>
<tr>
<td>Alexandre Foysey-Geoffroy</td>
<td>CERM</td>
<td>March 2010</td>
<td>Zeolites</td>
</tr>
<tr>
<td>Alice Peer</td>
<td>Newcastle U., Australia</td>
<td>July 2006</td>
<td>Methane combustion</td>
</tr>
<tr>
<td>Alessandro Zolin</td>
<td>Modena U., Italy</td>
<td>July 2008</td>
<td>PtOr/H systems</td>
</tr>
<tr>
<td>Andreas Heyden</td>
<td>South Carolina U.</td>
<td>May 2009</td>
<td>Prion/melanism</td>
</tr>
<tr>
<td>Anya Maria Marin</td>
<td>Université Nat. de Colombie</td>
<td>October 2007</td>
<td>Software development</td>
</tr>
<tr>
<td>Ananth Grama</td>
<td>Purdue U.</td>
<td>June 2007</td>
<td>Zn/O/water</td>
</tr>
<tr>
<td>Andrea Luisa da Rosa</td>
<td>U. Bremen</td>
<td>June 2009</td>
<td>V/H/BiO₃</td>
</tr>
<tr>
<td>Antonio Carmona</td>
<td>U. Palermo, Italy</td>
<td>May 2007</td>
<td>Polymers, fuel cells</td>
</tr>
<tr>
<td>Alex A. Kukhno</td>
<td>U. Uppsala, Sweden</td>
<td>February 2008</td>
<td>Protein/metal</td>
</tr>
<tr>
<td>Anis Oister</td>
<td>NASA/AMES</td>
<td>May 2006</td>
<td>NO· impact on Cenereais</td>
</tr>
<tr>
<td>Anatoly Belomoshow</td>
<td>U. Uppsala, Sweden</td>
<td>February 2006</td>
<td>H₂/0₃ shock</td>
</tr>
<tr>
<td>Ana Koester</td>
<td>Sandia National Labs</td>
<td>February 2005</td>
<td>SiO₂</td>
</tr>
<tr>
<td>Ashwini R. Manimaran</td>
<td>Caltech</td>
<td>April 2006</td>
<td>Mo dislocations</td>
</tr>
<tr>
<td>Brian Heinze</td>
<td>ARL, Maryland</td>
<td>August 2008</td>
<td>Ni/A/AO</td>
</tr>
<tr>
<td>Blas Pedro Umerena</td>
<td>Los Alamitos National Lab</td>
<td>June 2004</td>
<td>PAH-chusters</td>
</tr>
<tr>
<td>Angela Voito</td>
<td>U. Utah</td>
<td>April 2003</td>
<td>PAH-chusters</td>
</tr>
<tr>
<td>Camilo Calleron</td>
<td>U. Boston</td>
<td>November 2009</td>
<td>Gold</td>
</tr>
<tr>
<td>Catherine Tweedle</td>
<td>MIT</td>
<td>May 2007</td>
<td>Polymer surfaces</td>
</tr>
<tr>
<td>Changsoo Kim</td>
<td>Korea</td>
<td>April 2009</td>
<td>PDMAS/Ar</td>
</tr>
<tr>
<td>Christian Czichos</td>
<td>Colorado State of Mines</td>
<td>October 2007</td>
<td>US Naval Academy</td>
</tr>
<tr>
<td>Christian Wu</td>
<td>LLNL</td>
<td>June 2010</td>
<td>US Navy Academy</td>
</tr>
<tr>
<td>Christopher Strickland</td>
<td>Pacific Northwest National Lab</td>
<td>April 2007</td>
<td>ENS Lyon</td>
</tr>
<tr>
<td>Chun-Wei Pao</td>
<td>Los Alamitos National Lab</td>
<td>November 2009</td>
<td>Inst. For Plasma Res. India</td>
</tr>
<tr>
<td>David Curvelle-Perre</td>
<td>Total, Coal</td>
<td>September 2009</td>
<td>Pacific Northwest National Lab</td>
</tr>
<tr>
<td>Daniel Frase</td>
<td>U. Bremen, Germany</td>
<td>March 2007</td>
<td>U. Palermo</td>
</tr>
<tr>
<td>Daniil Bedrov</td>
<td>Air Force Research Labs</td>
<td>September 2006</td>
<td>Sandy National Labs</td>
</tr>
<tr>
<td>Donald Phelps</td>
<td>University of London</td>
<td>September 2008</td>
<td>LNL</td>
</tr>
<tr>
<td>Dongshen Wang</td>
<td>U. Delaware</td>
<td>July 2007</td>
<td>Rob Riggelman</td>
</tr>
<tr>
<td>Donghsun Wang</td>
<td>U. Delaware</td>
<td>May 2006</td>
<td>Rui Zhan</td>
</tr>
<tr>
<td>Eduardo Bringa</td>
<td>Livermore National Labs</td>
<td>June 2006</td>
<td>Rui Zhan</td>
</tr>
<tr>
<td>Chingshuang Tang</td>
<td>U. Colorado</td>
<td>January 2010</td>
<td>Rui Zhan</td>
</tr>
<tr>
<td>Edinah I.</td>
<td>U. Florida</td>
<td>June 2006</td>
<td>Rui Zhan</td>
</tr>
<tr>
<td>Erik Santiso</td>
<td>North Carolina, USA</td>
<td>July 2007</td>
<td>Rui Zhan</td>
</tr>
<tr>
<td>Ferdinando Fanoo</td>
<td>ITP, France</td>
<td>February 2006</td>
<td>Hydrocarbons</td>
</tr>
<tr>
<td>Feng Chen</td>
<td>China U.</td>
<td>November 2009</td>
<td>Nanodiamonds/collapsing</td>
</tr>
<tr>
<td>Francesco Ferrante</td>
<td>ITP, France</td>
<td>February 2004</td>
<td>CNH/0/water</td>
</tr>
<tr>
<td>Fidel Valga</td>
<td>U. Colorado</td>
<td>June 2006</td>
<td>Hydrocarbons</td>
</tr>
<tr>
<td>John Duly</td>
<td>Rice University</td>
<td>June 2006</td>
<td>Cellulose</td>
</tr>
<tr>
<td>Feng Wang</td>
<td>U. Boston</td>
<td>July 2007</td>
<td>CNT growth on Ni</td>
</tr>
<tr>
<td>Joel Fried</td>
<td>U. Dayton</td>
<td>July 2007</td>
<td>Water</td>
</tr>
<tr>
<td>R.J.M. Konings</td>
<td>Inst.of TransU., Germany</td>
<td>August 2005</td>
<td>Phosphates</td>
</tr>
<tr>
<td>Gerrit Stengen</td>
<td>Oak Ridge National Lab</td>
<td>April 2010</td>
<td>Si/SiO₂ clusters</td>
</tr>
<tr>
<td>German Sanyoluk</td>
<td>Oak Ridge National Lab</td>
<td>June 2010</td>
<td>DNA polymers/kmetal</td>
</tr>
<tr>
<td>Guillaume Marois</td>
<td>U. New Mexico</td>
<td>May 2007</td>
<td>Water clusters</td>
</tr>
<tr>
<td>Harald Bergham</td>
<td>U. Bergen, Germany</td>
<td>November 2007</td>
<td>Hydrocarbon oxidation</td>
</tr>
<tr>
<td>Markus Bachler</td>
<td>U. Stuttgart, Germany</td>
<td>December 2008</td>
<td>Protein/PE interface</td>
</tr>
<tr>
<td>Mats Lofqvist</td>
<td>UNICAMP, Brazil</td>
<td>August 2005</td>
<td>Crack propagation</td>
</tr>
<tr>
<td>Peter Lofqvist</td>
<td>MIT</td>
<td>August 2005</td>
<td>W/COC</td>
</tr>
<tr>
<td>Magnus Madsen</td>
<td>U. Graz</td>
<td>July 2008</td>
<td>HE-materials</td>
</tr>
<tr>
<td>Michael Meserski</td>
<td>UC Riverside, CA</td>
<td>October 2005</td>
<td>Zn/NO</td>
</tr>
<tr>
<td>Michael Paraskevadis</td>
<td>Union University</td>
<td>January 2007</td>
<td>P/O Union</td>
</tr>
<tr>
<td>Michael Paschek</td>
<td>Livermore National Lab</td>
<td>January 2004</td>
<td>Force field development</td>
</tr>
<tr>
<td>Monika Winter</td>
<td>Winterbrugg, Norway</td>
<td>April 2007</td>
<td>High-energy materials</td>
</tr>
<tr>
<td>Nicholas Winter</td>
<td>University of Bergen, Norway</td>
<td>July 2008</td>
<td>High-temperature methane</td>
</tr>
<tr>
<td>Oliver Poliarcia</td>
<td>Inst. Centro de Bourgogne</td>
<td>February 2005</td>
<td>Water systems</td>
</tr>
<tr>
<td>Paul Kost</td>
<td>ORNL</td>
<td>May 2005</td>
<td>Carbon/Li interactions</td>
</tr>
<tr>
<td>Paul Matthews</td>
<td>US Naval Academy</td>
<td>October 2007</td>
<td>Amorphous carbon</td>
</tr>
<tr>
<td>Philip Staut</td>
<td>ENS Lyon</td>
<td>February 2005</td>
<td>Nitrogen carbons</td>
</tr>
<tr>
<td>Poonam Deshpande</td>
<td>Inst. For Plasma Res. India</td>
<td>September 2005</td>
<td>Hydrocarbons</td>
</tr>
<tr>
<td>Ram Devanathan</td>
<td>Pacific Northwest National Lab</td>
<td>October 2009</td>
<td>Proton transfer/TeO₂</td>
</tr>
<tr>
<td>Remoges Cepose</td>
<td>US Naval Academy</td>
<td>August 2009</td>
<td>Zn/MOF</td>
</tr>
<tr>
<td>Rene van Githoven</td>
<td>Sandia National Labs</td>
<td>February 2005</td>
<td>Si/SiO₂ interfaces</td>
</tr>
<tr>
<td>Reinhard Mann</td>
<td>LNL</td>
<td>June 2010</td>
<td>Fluorohydrocarbons</td>
</tr>
<tr>
<td>Rob Riggelman</td>
<td>Stony Brook University</td>
<td>August 2004</td>
<td>Organosilicates</td>
</tr>
<tr>
<td>Robert H. Miller</td>
<td>University of Amsterdam</td>
<td>January 2010</td>
<td>Protein/water</td>
</tr>
<tr>
<td>Rui Zhan</td>
<td>Sandia National Labs</td>
<td>April 2007</td>
<td>Software development</td>
</tr>
<tr>
<td>Ruben Rizzi</td>
<td>Aachen University</td>
<td>October 2009</td>
<td>Proteins</td>
</tr>
<tr>
<td>Rui Zhan</td>
<td>Tokyo Tech, Singapore</td>
<td>February 2005</td>
<td>Au/SiCH interactions</td>
</tr>
<tr>
<td>Satoru Iwamoto</td>
<td>Tsukuba University</td>
<td>August 2008</td>
<td>Si/SiO₂ impact</td>
</tr>
<tr>
<td>Serge Shvetski</td>
<td>U.S. Army</td>
<td>February 2005</td>
<td>YO/Si systems</td>
</tr>
<tr>
<td>Silvia Neese</td>
<td>U. Melbourne</td>
<td>March 2007</td>
<td>Hydrocarbon oxidation</td>
</tr>
<tr>
<td>Simon Morin</td>
<td>Oregon State University</td>
<td>August 2009</td>
<td>Hydrocarbon oxidation</td>
</tr>
<tr>
<td>Song Chang</td>
<td>A. Michigan</td>
<td>February 2005</td>
<td>Hydrocarbon oxidation</td>
</tr>
<tr>
<td>Sophia Garaschuk</td>
<td>U. South Carolina</td>
<td>May 2007</td>
<td>MOS/BAND</td>
</tr>
<tr>
<td>Stephan van Gisbergen</td>
<td>SCM (ADF/BAND)</td>
<td>November 2007</td>
<td>CEA, France</td>
</tr>
<tr>
<td>Philippe Simonetti</td>
<td>U. of Aarhus</td>
<td>December 2008</td>
<td>SPOF</td>
</tr>
<tr>
<td>Saumit Ghoshin</td>
<td>U. of Michigan</td>
<td>August 2005</td>
<td>SCRIPPS, Korea</td>
</tr>
<tr>
<td>Sibiru Akber</td>
<td>U. of Oregon</td>
<td>July 2008</td>
<td>U. Wisconsin</td>
</tr>
<tr>
<td>Soni Tullyani</td>
<td>U. of Massachusetts</td>
<td>October 2005</td>
<td>U. of Oxford, UK</td>
</tr>
<tr>
<td>Thomas Schoofelder</td>
<td>TU Chemnitz</td>
<td>July 2008</td>
<td>U. of Wisconsin</td>
</tr>
<tr>
<td>Tae Hyun Lee</td>
<td>NamYang Tech, Singapore</td>
<td>February 2005</td>
<td>U. of Wisconsin</td>
</tr>
<tr>
<td>Tiffany Cui</td>
<td>Texas A&amp;M University</td>
<td>Texas A&amp;M</td>
<td>U. of Missouri</td>
</tr>
<tr>
<td>Tung-Ching Hsu</td>
<td>TU Eindhoven, Holland</td>
<td>September 2005</td>
<td>U. of Missouri</td>
</tr>
<tr>
<td>Tsinghua University</td>
<td>Tongji University, Shanghai</td>
<td>September 2005</td>
<td>U. of Missouri</td>
</tr>
<tr>
<td>U. of Virginia</td>
<td>TU Eindhoven, Holland</td>
<td>August 2004</td>
<td>U. of Missouri</td>
</tr>
<tr>
<td>U. of Virginia</td>
<td>TU Eindhoven, Holland</td>
<td>April 2007</td>
<td>U. of Missouri</td>
</tr>
<tr>
<td>U. of Virginia</td>
<td>TU Eindhoven, Holland</td>
<td>October 2009</td>
<td>Water clusters</td>
</tr>
<tr>
<td>U. of Virginia</td>
<td>TU Eindhoven, Holland</td>
<td>February 2008</td>
<td>Water clusters</td>
</tr>
</tbody>
</table>

### 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.

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)

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

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

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

- 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

Database of reaction kinetics and diffusion constants
Force field development: hydrocarbon oxidation

Oxidation reactions

Radical rearrangements

Rotational barriers

Angle strain

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

- total training set contains about 1700 compounds
Test ReaxFF CHO-description: oxidation of o-xylene

- Oxidation initiates with OOH-formation
- Final products dominated by CO, CO₂ and H₂O

Consumed O₂

CO₂

H₂O

CO

O-xylene

OOH

OH

-Chenoweth, van Duin and Goddard, JPC-A 2008
- Reaction initiation with HO₂- formation

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

- Only after H₂C=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 CO₂, H₂O and CO

-ReaxFF gives sensible predictions for the o-Xylene oxidation mechanism.

- This mechanism can be further validated against QM
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
Sulfur Effects on pyrolysis

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

Simulation of coal combustion in the presence of a MoNi alloy reactor wall

- 50,000 atoms, 4 processors
- Enables us to study the chemistry at the reactor wall surface
- Study formation of oxide layer, catalytic conversion of coal
- Study long-term chemical and physical transformations in wall structure.
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

Water dimers

- QM
- ReaxFF

Other data in training set:
- H-O-H bond dissociation
- H-O-H angle distortion
- Ice(cmc) equation of state
- Mulliken charges for water clusters
- Water vibrational frequencies
- H-H, O=O and HO-OH bond dissociation

Water clusters

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

QM

ReaxFF

Neutral
Auto- and Cu-assisted ionization of water

- 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

Density, cohesive energy

Radial distribution

Diffusion constant

800 water box

- NIST: $\Delta H_{\text{vap}} = 10.5$ kcal/mol
- Reax: $\Delta H_{\text{vap}} = 10.9$ kcal/mol

- NIST: $\delta = 0.2272$ Å²/ps
- Reax: $\delta = 0.2106$ Å²/ps

Eisenberg and Kauzman, Oxford Univ. Press 1969

Zeolite growth

ReaxFF for water

Pt/Ni fuel cells

Nafion fuel cell

Dendrimers/metal cations

Enzymes/DNA/organic catalysis

Phosphates/sulfonates

Amines/carboxylate pKa

Jahn-Teller distorted

Cu(H_2O)_6^{2+}-cluster

Cu/Zn oxides

With Raymand & Hermannsson (Uppsala)

With Trinh & van Santen (Eindhoven)

With Ram Devanathan (PNNL))

With Ramie & Doren (Delaware)

ZnO/H_2O Partially hydroxyl covered surface

MD(300K)

5Si(OH)_4+OH^- \rightarrow Si_5O_{15}H_9+6H_2O

Restrained dynamics

H_2O_2

MP2/6-31G(\ddagger) ReaxFF

\Delta E(kcal/mol)

\Delta G(kcal/mol)

n=1,2,3,4

AH_2(H_2O)_n

A:+H^+(H_2O)_n

n=1

n=2

n=3

n=4
Simulations of water dissociation on zinc oxide surfaces

Collaborators: David Raymand and Kersti Hermannsson (Uppsala)

B3LYP and ReaxFF equations of state for ZnO-cystal configurations

Bulk equations of state

Water dissociation barriers

Raymand, van Duin, van Duin, Baudin and Hermannsson, Surface Science 2008
Raymand, van Duin, Goddard and Hermannsson, 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 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
Application to cold welding of gold surfaces

With Kaushik Joshi

- 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.

Simulation of the energy release during interface formation

Influence of oxidation on surface cohesion

Joshi, van Duin and Jacob, J.Mat. Chem., 2010
Keith, Fantauzzi, Jacob and van Duin, PRB 2010
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 $\text{V}_2\text{O}_5$ 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

Engineering

ReaxFF

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

- Interface properties
- Reaction kinetics
- Diffusion constants
- Excellent agreement between ReaxFF and QM for entire reaction path
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

Metal particle catalysis: Hexane cracking on Fe-clusters

With Kaushik Joshi; preliminary results

Hexane with Fe$_{13}$ particles, T=1750K
- 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.
Acknowledgments

Collaborators:
- Jonathan Mathews, Jim Kubicki and Mike Janik (Penn State)
- David Raymand and Kersti Hermannson (Uppsala)
- Kimberley Chenoweth, Vyacheslav Bryantsev and Bill Goddard (Caltech)
- Aidan Thompson, Steve Plimpton (Sandia), Metin Aktulga (Purdue), Stan van Gisbergen (SCM) (parallel MD)

Funding:
- PSU/KISK startup grant #C000032472
- Illinois Coal grant ICCI 10/7B-3
- NSF (TiO₂/water)
- AFOSR/SBIR (Hydrocarbon cracking)
- DoD/STTR (rubber oxidation)
- British Royal Society (initial ReaxFF funding)

More information:
Website: http://www.engr.psu.edu/adri
Office: 136 Research East
Phone: 814-863-6277
E-mail: acv13@psu.edu

Parallel ReaxFF simulation of hydrocarbon cracking (4800 atoms, 4 processors)