

# Applications of the ReaxFF reactive force field for identifying properties for complex materials and interfaces

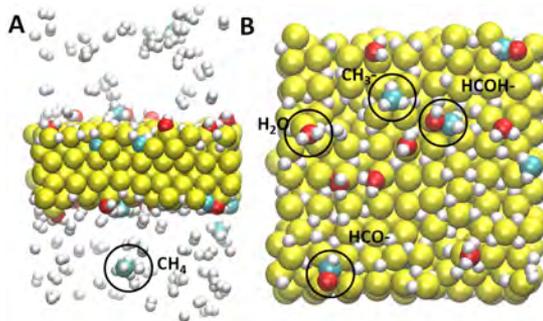
Adri van Duin

Professor & CTO

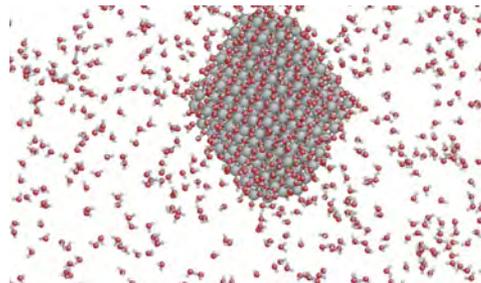
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ReaxFF simulations of Fischer-Tropsch catalysis on a Fe-metal surface (Zou et al. Topics in Catalysis 2012)



ReaxFF structure of a  $\text{TiO}_2$  nanoparticle in water (Raju et al. Nano Letters 2014)

NSCCSADF ReaxFF  
Workshop, London

September 27 2016

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# Current Penn State group members and projects



## Postdoctoral staff

Dr. Yun-Kyung Shin  
Dr. Mark Fedkin  
Dr. Weiwei Zhang  
Dr. Roghayyeh Lofti

Metal alloys, Sulfur-embrittlement, Proteins  
Mineral dissolution in water/electrolyte systems  
Fuel cells, proton transfer  
Tribology

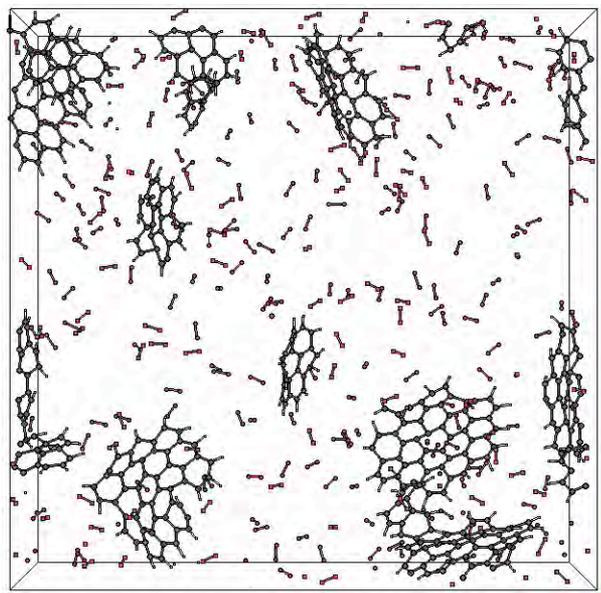
## PhD-students

Mahbub Islam  
Chowdhury Ashraf  
Kichul Yoon  
ASM Jonayat  
Abhishek Jain  
Seung Ho Hahn  
Gunwoo Jo  
Behzad Damirchi

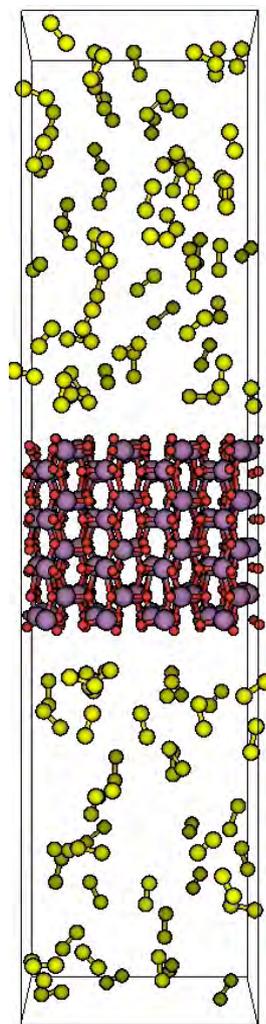
Li/S battery interface simulations  
Combustion  
Electrocatalysis, graphene surface chemistry  
Mixed metal oxide catalysis  
Atomistic and continuum scale combustion  
Tribochemistry  
2D-materials  
Biomaterials

# Outline

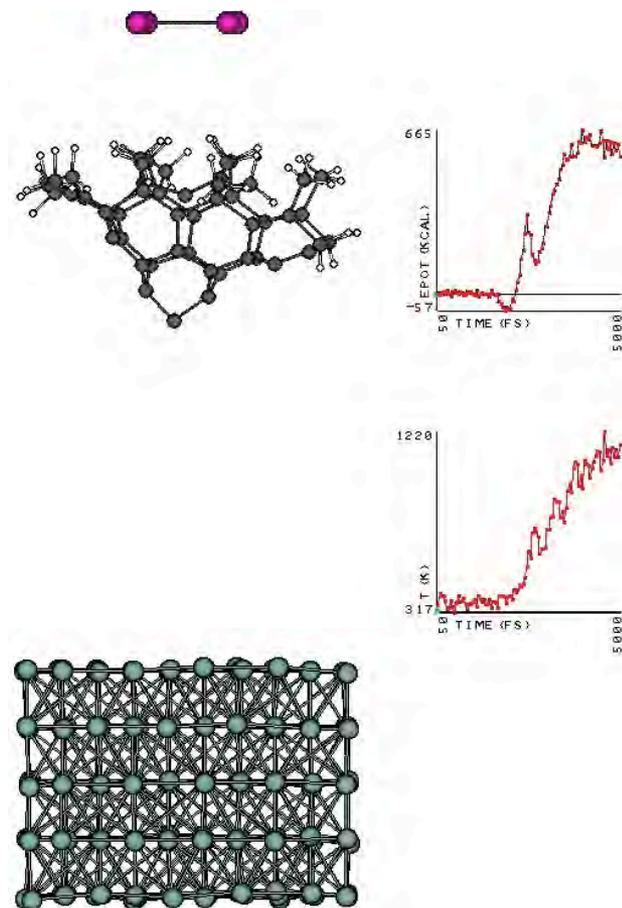
- The ReaxFF reactive force field
- Overview of ReaxFF applications
- Tribochemistry applications
- Proton transport across graphene
- New and ongoing developments
- Summary



ReaxFF MD simulation  
of char combustion at  
T=2500K



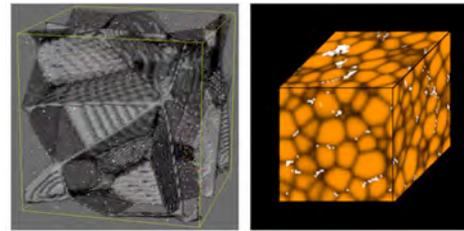
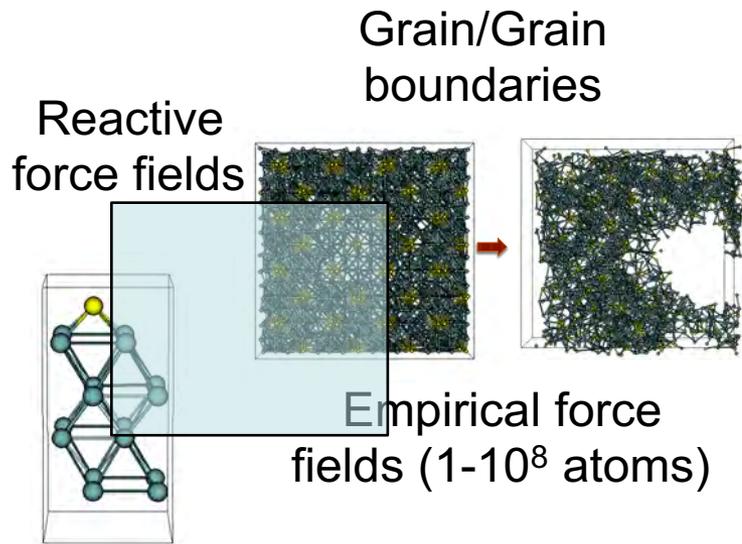
ReaxFF MD simulation  
of S<sub>2</sub> gas reacting with a  
MoO<sub>3</sub> slab at T=1000K



ReaxFF MD simulation of the  
indentation of a Ni-slab with a  
diamond fragment (Tavazza et al.,  
*J.Phys.Chem C* 2016, **119**, 13580)

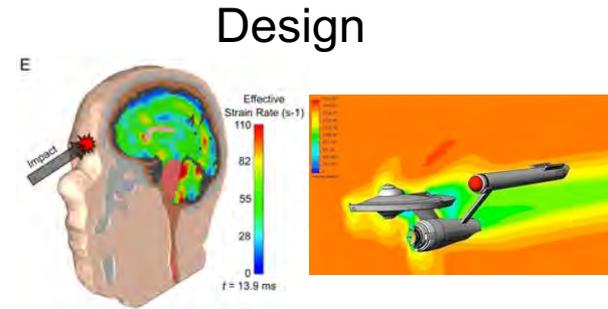
# Length scales in Material Computation

## Reactive force fields

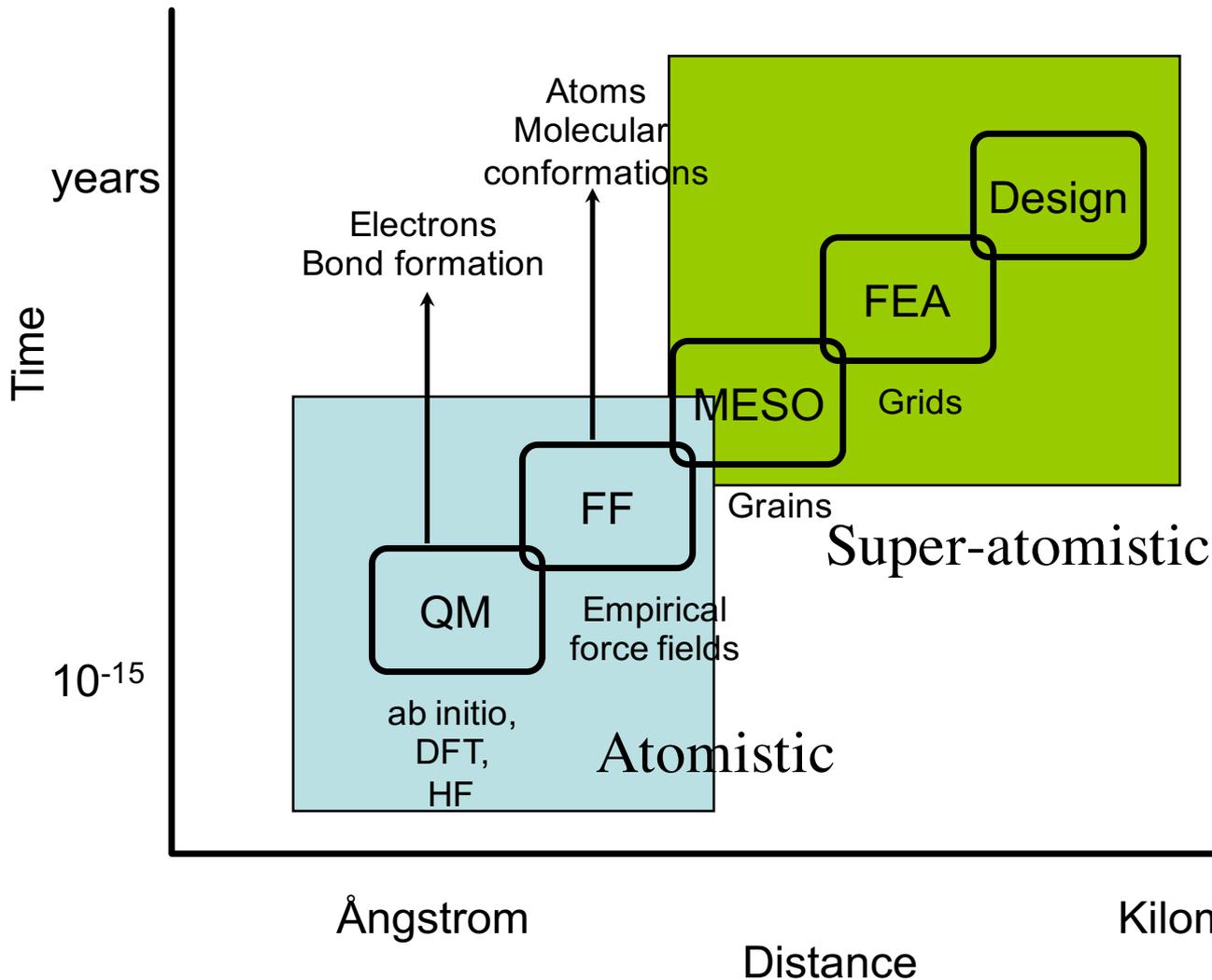


Multigrain

Phase field,  
CALPHAD



# Simulations on the dynamics of chemical reactions



QM methods:  
- Fundamental  
- Expensive, only small systems

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

# QM-methods

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

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

Kinetic energy

Nucleus-Nucleus repulsion

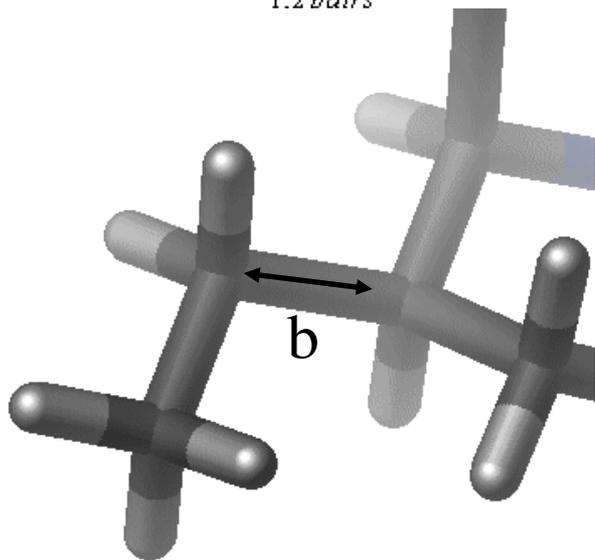
Nucleus-Electron attraction

Electron-Electron repulsion  
(analytically unsolvable)

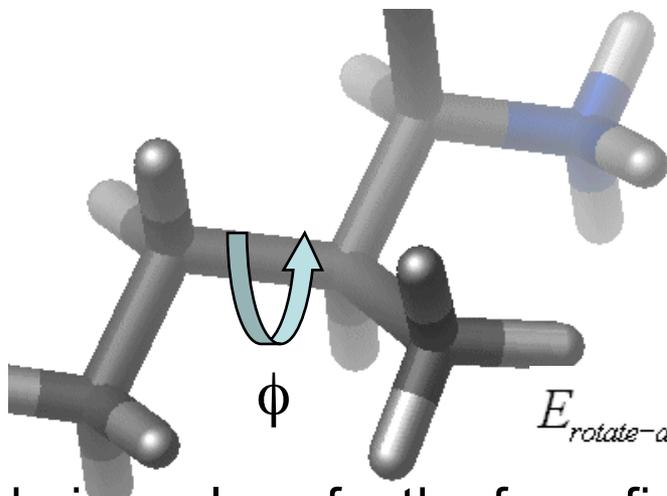
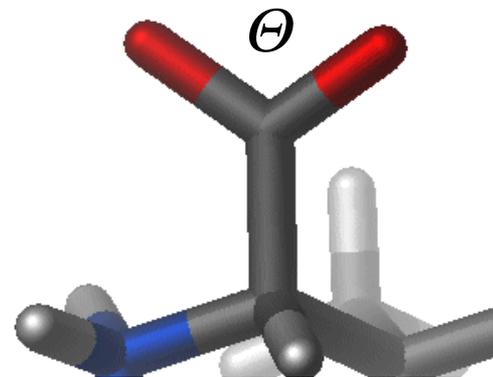
- Allows calculation of atomic interactions First Principles
- Computationally expensive, especially for finding accurate approximations of electron-electron repulsion term

# Force field methods

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



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

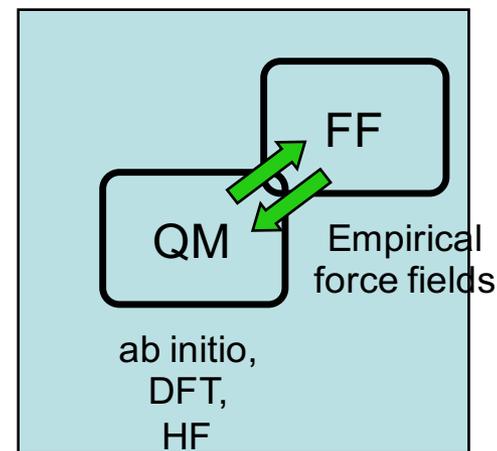


$$E_{\text{rotate-along-bond}} = \sum_{1,4 \text{ pairs}} K_\phi (1 - \cos(n\phi))$$

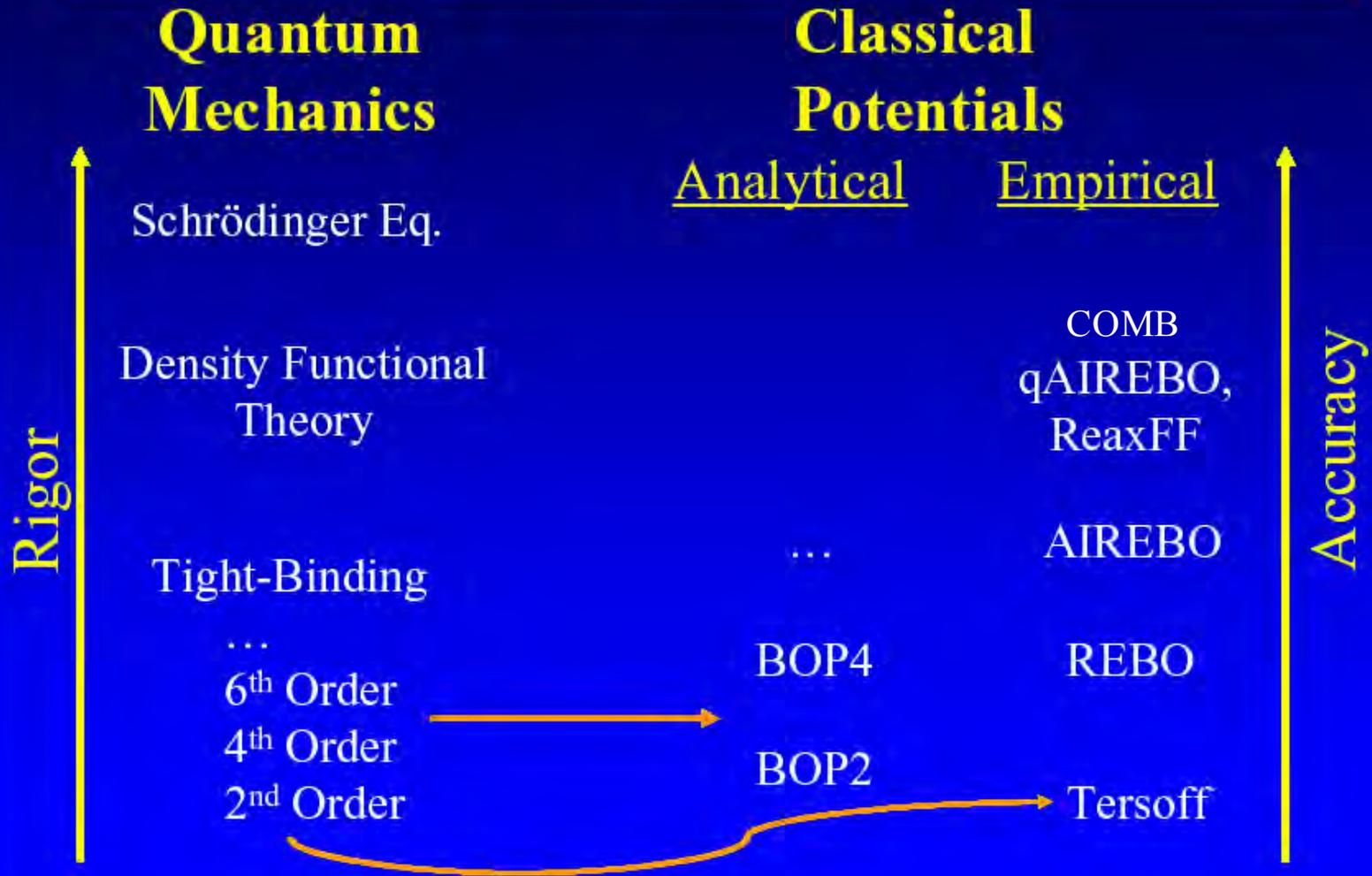
- Empirical, we need to derive values for the force field parameters (intuition, compare to experiment, compare to QM)
- MUCH faster than QM; can be applied to bigger systems

# QM and FF-based approaches to reactive MD

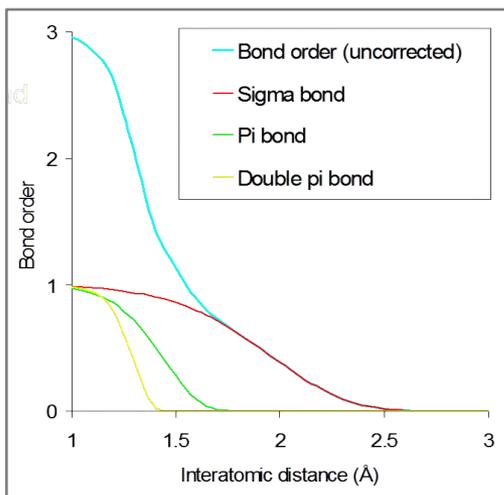
- Option 1: Burn CPUs with QM/MD (e.g. Raty et al., PRL 2005, Wang et al. Nature Chem 2014)
- Option 2: use empirical assumptions to make QM faster (semi-empirical methods)
  - CINDO/MINDO/AM1/MOPAC (e.g. Pople and Segal, JCP 1966; Stewart, J. Comp. Chem. 1989)
  - Tight-binding (e.g. McMahan and Klepeis, PRB 1997)
  - Analytical Bond Order Potentials (e.g. Pettifor and Oleinik, PRB 1999)
- Option 3: Add ability to simulate reactions to FF-method (empirical bond-order based force fields)
  - Tersoff/Brenner /AIREBO (Tersoff, PRL 1988; Brenner, PRB 1990, Stuart et al., JCP 2000)
  - LCBOP (de Los et al., PRB 2005)
  - EDIP (e.g. Bazant and Kaxiras, PRL 1996)
  - COMB (e.g. Liang et al. JPC-A 2012)
  - ReaxFF (e.g. van Duin et al. JPC-A 2001)



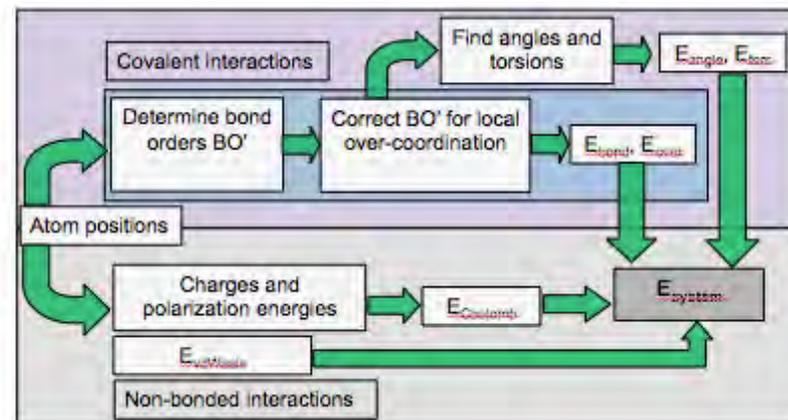
# Classes of Models



# Key Features of ReaxFF

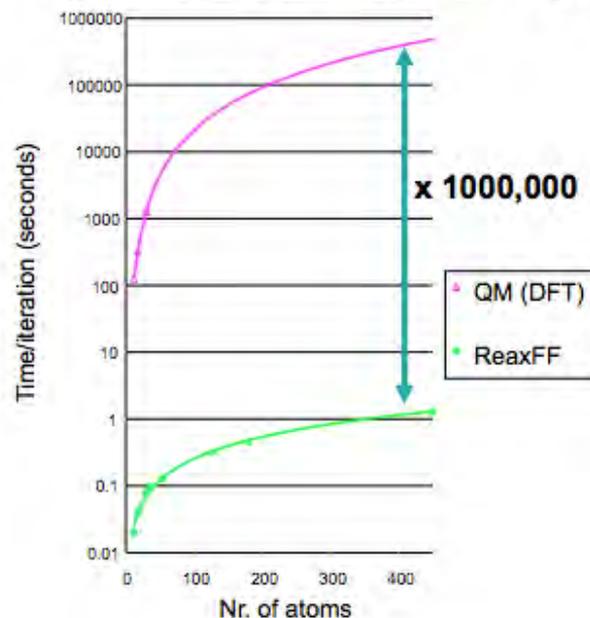


$$BO_{ij} = \exp \left[ p_{bo,1} \cdot \left( \frac{r_{ij}}{r_o^\sigma} \right)^{p_{bo,2}} \right] + \exp \left[ p_{bo,3} \cdot \left( \frac{r_{ij}}{r_o^\pi} \right)^{p_{bo,4}} \right] + \exp \left[ p_{bo,5} \cdot \left( \frac{r_{ij}}{r_o^{\pi\pi}} \right)^{p_{bo,6}} \right]$$



- To get a smooth transition from nonbonded to single, double and triple bonded systems ReaxFF employs a bond length/bond order relationship<sup>1,2,3</sup>. Bond orders are updated in every iteration
- All connectivity-dependent interactions (i.e. valence and torsion angles) are made bond-order dependent.
- Nonbonded interactions (van der Waals, Coulomb) are calculated between every atom pair

$$E_{system} = E_{bond} + E_{val} + E_{tors} + E_{vdWaal} + E_{Coulomb} + E_{over} + E_{under}$$

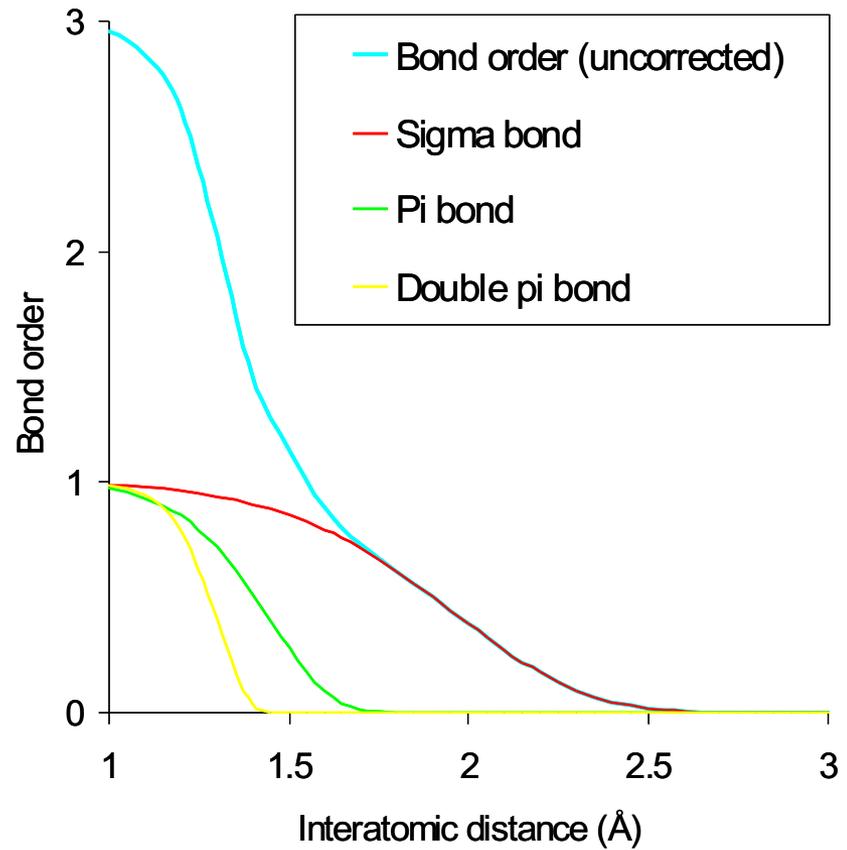


ReaxFF allows for reactive MD-simulations on systems containing more than 1000 atoms

# Introduction of bond orders

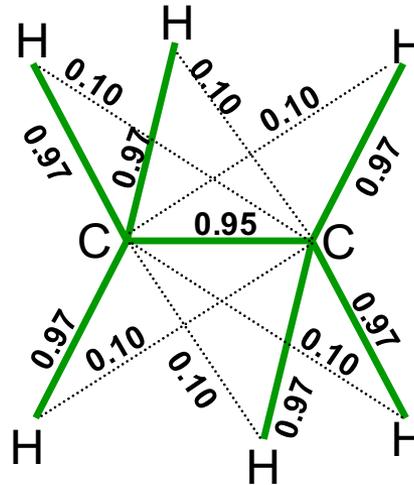
Calculation of bond orders from interatomic distances

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



# Bond order correction

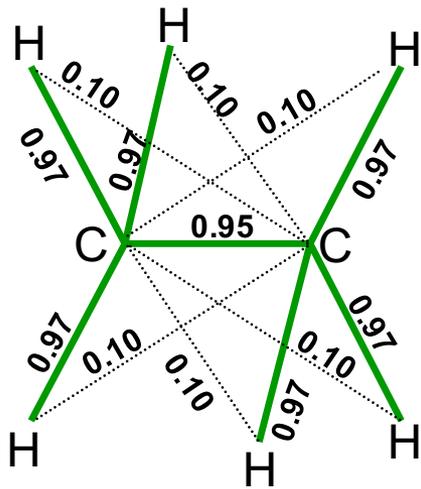
Uncorrected bond orders in ethane



$$\sum \text{BO}_C = 4.16$$

$$\sum \text{BO}_H = 1.17$$

- Unphysical; normally coordinated atoms should not have binding interactions with next-neighbours
- Puts strain on angle and overcoordination potentials
- Short-range bond orders will not capture transition states



Corrected bond orders

Uncorrected bond orders

$$BO_{ij}^{\sigma} = BO_{ij}^{\sigma} \cdot f_1(\Delta_i, \Delta_j) \cdot f_4(\Delta_i, BO_{ij}^{\sigma}) \cdot f_5(\Delta_j, BO_{ij}^{\sigma})$$

$$BO_{ij}^{\pi} = BO_{ij}^{\pi} \cdot f_1(\Delta_i, \Delta_j) \cdot f_1(\Delta_i, \Delta_j) \cdot f_4(\Delta_i, BO_{ij}^{\pi}) \cdot f_5(\Delta_j, BO_{ij}^{\pi})$$

$$BO_{ij}^{\pi\pi} = BO_{ij}^{\pi\pi} \cdot f_1(\Delta_i, \Delta_j) \cdot f_1(\Delta_i, \Delta_j) \cdot f_4(\Delta_i, BO_{ij}^{\pi\pi}) \cdot f_5(\Delta_j, BO_{ij}^{\pi\pi})$$

$$BO_{ij} = BO_{ij}^{\sigma} + BO_{ij}^{\pi} + BO_{ij}^{\pi\pi}$$

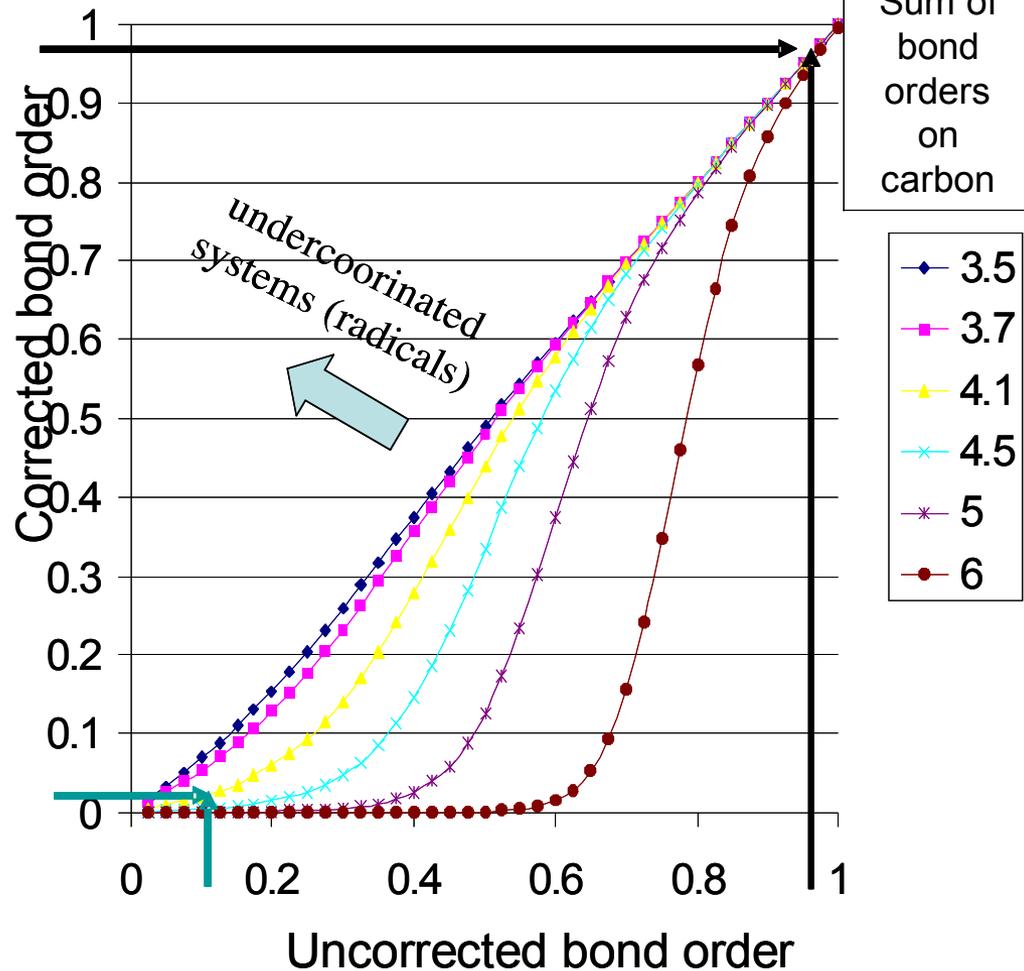
$$\Delta_i^{boc} = -Val_i^{boc} + \sum_{j=1}^{neighbours(i)} BO_{ij}^{\sigma}$$

$$f_1(\Delta_i, \Delta_j) = \frac{1}{2} \cdot \left( \frac{Val_i + f_2(\Delta_i, \Delta_j)}{Val_i + f_2(\Delta_i, \Delta_j) + f_3(\Delta_i, \Delta_j)} + \frac{Val_j + f_2(\Delta_i, \Delta_j)}{Val_j + f_2(\Delta_i, \Delta_j) + f_3(\Delta_i, \Delta_j)} \right)$$

$$f_2(\Delta_i, \Delta_j) = \exp(-p_{boc1} \cdot \Delta_i) + \exp(-p_{boc1} \cdot \Delta_j)$$

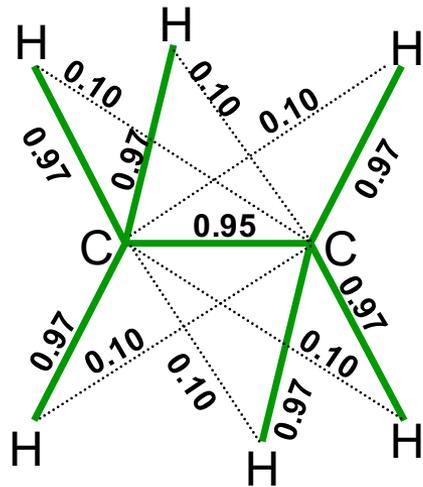
$$f_3(\Delta_i, \Delta_j) = -\frac{1}{p_{boc2}} \cdot \ln \left\{ \frac{1}{2} \cdot \left[ \exp(-p_{boc2} \cdot \Delta_i) + \exp(-p_{boc2} \cdot \Delta_j) \right] \right\}$$

$$f_4(\Delta_i, BO_{ij}^{\sigma}) = \frac{1}{1 + \exp(-p_{boc3} \cdot (p_{boc4} \cdot BO_{ij}^{\sigma} \cdot BO_{ij}^{\sigma} - \Delta_i^{boc}) + p_{boc5})}$$



- Normally coordinated carbon will not make weak bonds, under-coordinated carbon (radical) can make weak bonds (no correction)

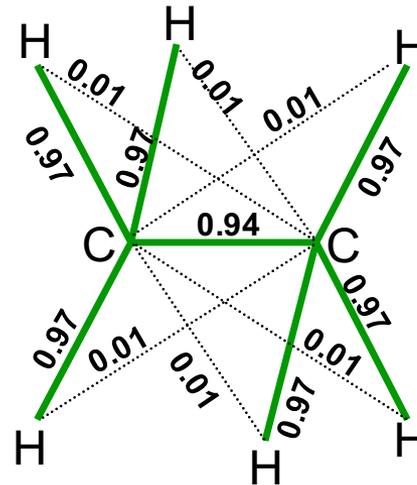
Uncorrected bond orders



$$\sum BO_C = 4.16$$

$$\sum BO_H = 1.17$$

Corrected bond orders

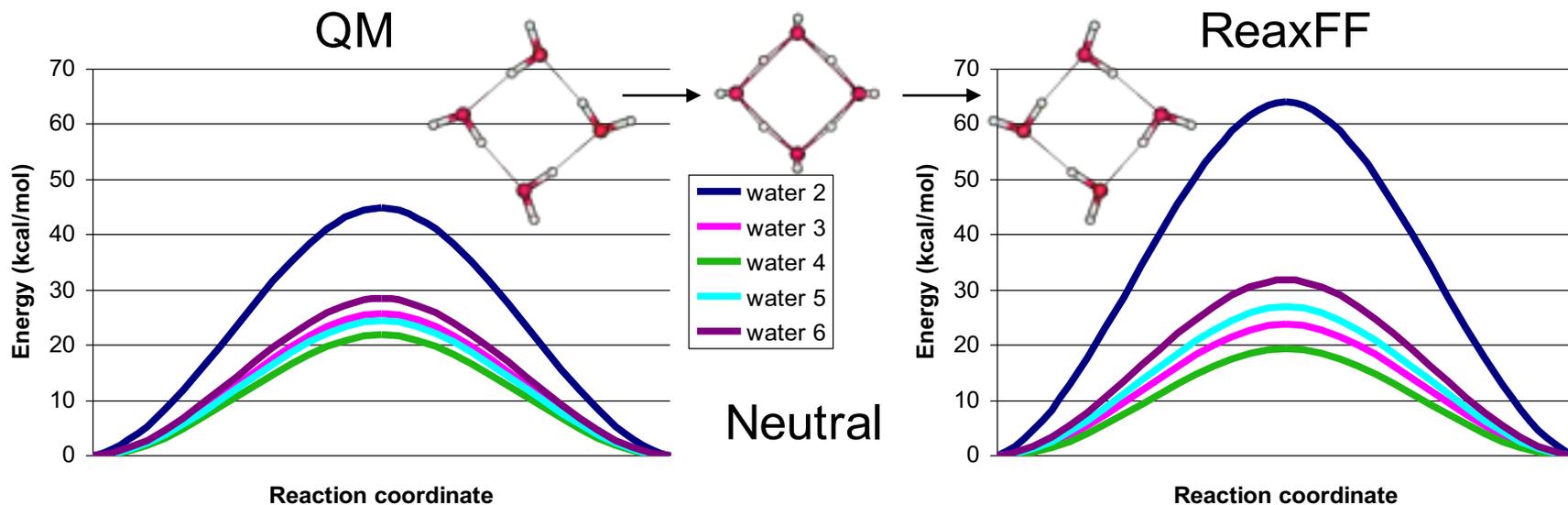


$$\sum BO_C = 3.88$$

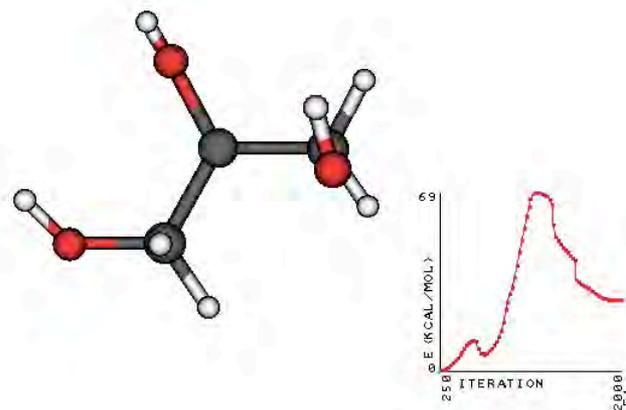
$$\sum BO_H = 0.98$$

- Correction removes unrealistic weak bonds but leaves strong bonds intact
- Increases computational expense as bond orders become multibody interactions
- Correction only applied for covalent-systems, not for metals

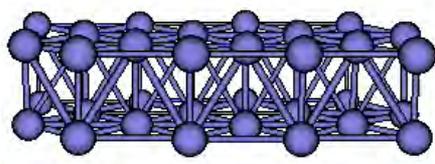
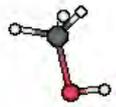
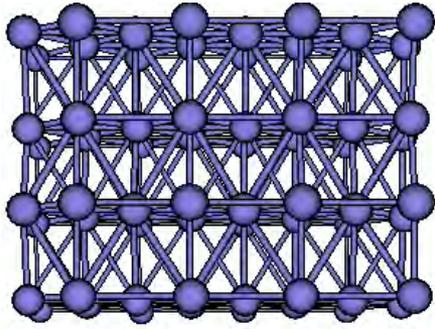
# Reaction barriers for concerted reactions



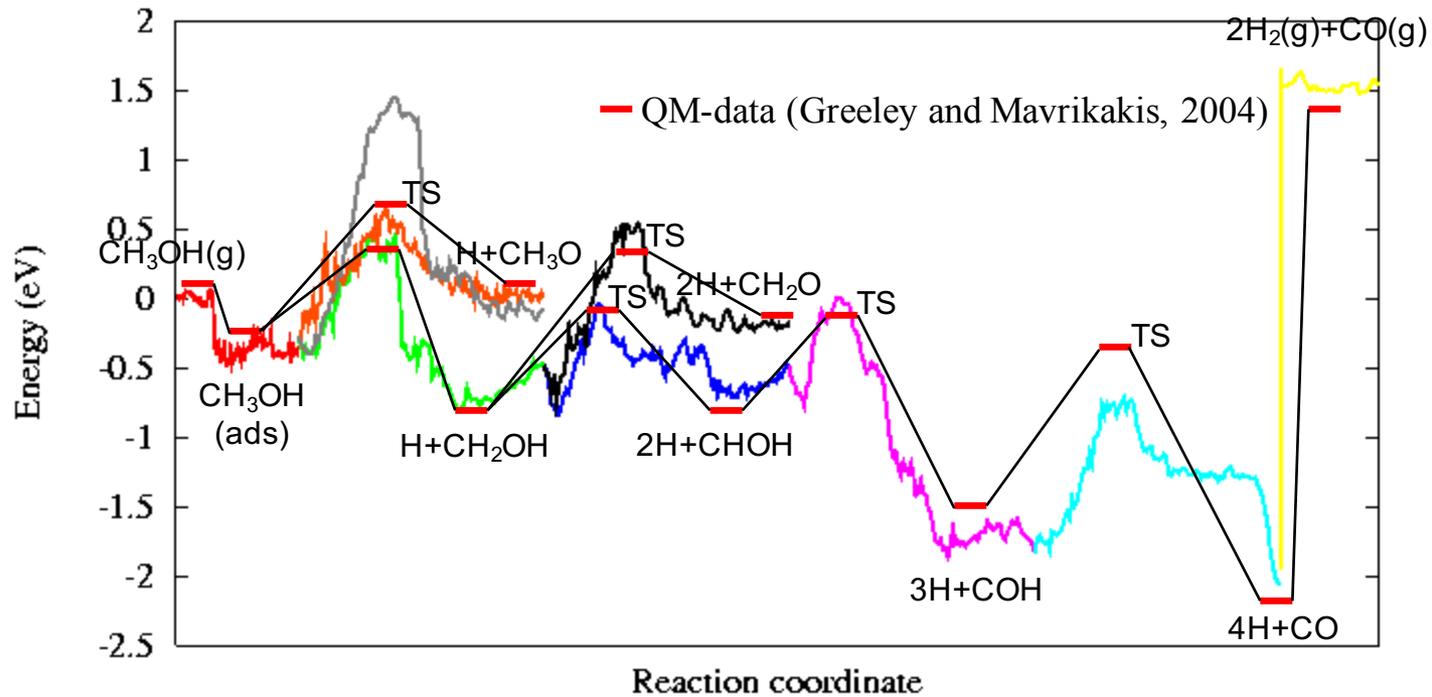
ReaxFF barrier for Grob fragmentation (collaboration with John Daily, Boulder). QM barrier: 65 kcal/mol (Nimlos et al., JPC-A 2006)



# Surface reactions



Methanol reaction on Pt[111]surface



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

- Good agreement between ReaxFF and QM for entire reaction path

# Charge polarization

- Assign one electronegativity and hardness to each element; optimize these parameters against QM-charge distributions
- Use system geometry in solving electronegativity equilibration equations in every iteration

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

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

.....

.....

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

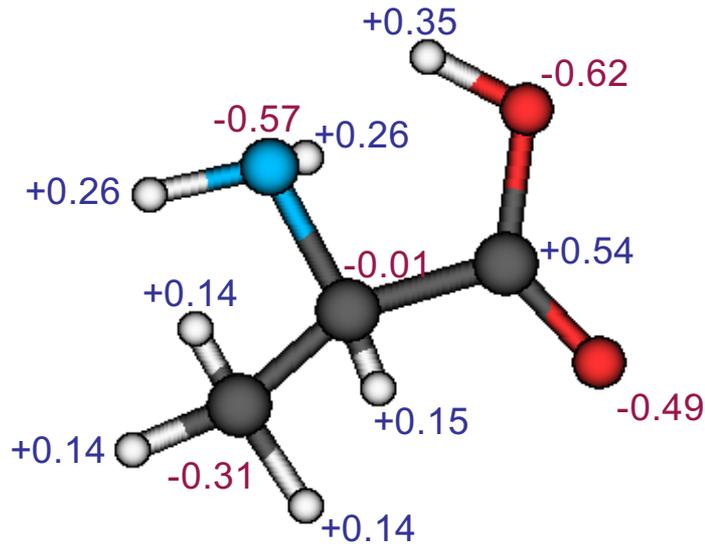
$$\sum_{i=1}^n q_i = 0$$

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

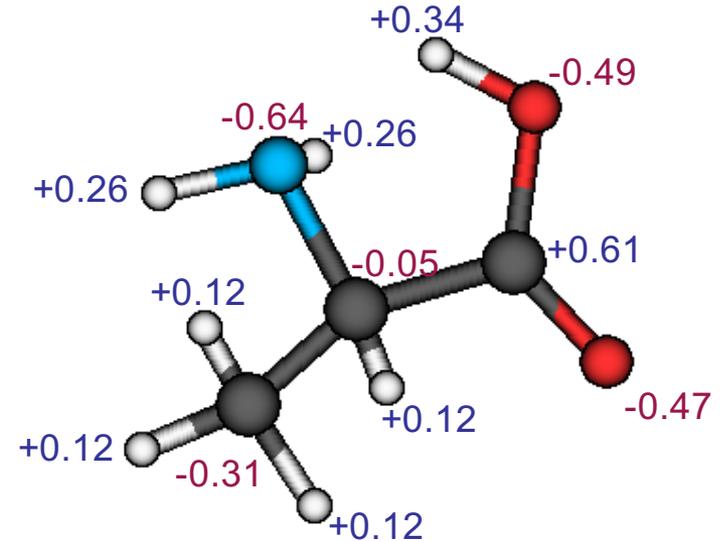
Similar to Qeq-method  
(Rappe and Goddard, J.  
Phys. Chem. 1991) with  
empirical shielding  
correction.

$\chi$ : atom electronegativity
$\eta$ : atom hardness
$\gamma$ : shielding parameter
$r$ : interatomic distances
$q$ : atom charge

ReaxFF charges



QM  
Mulliken charges  
DFT; 6-31G\*\*

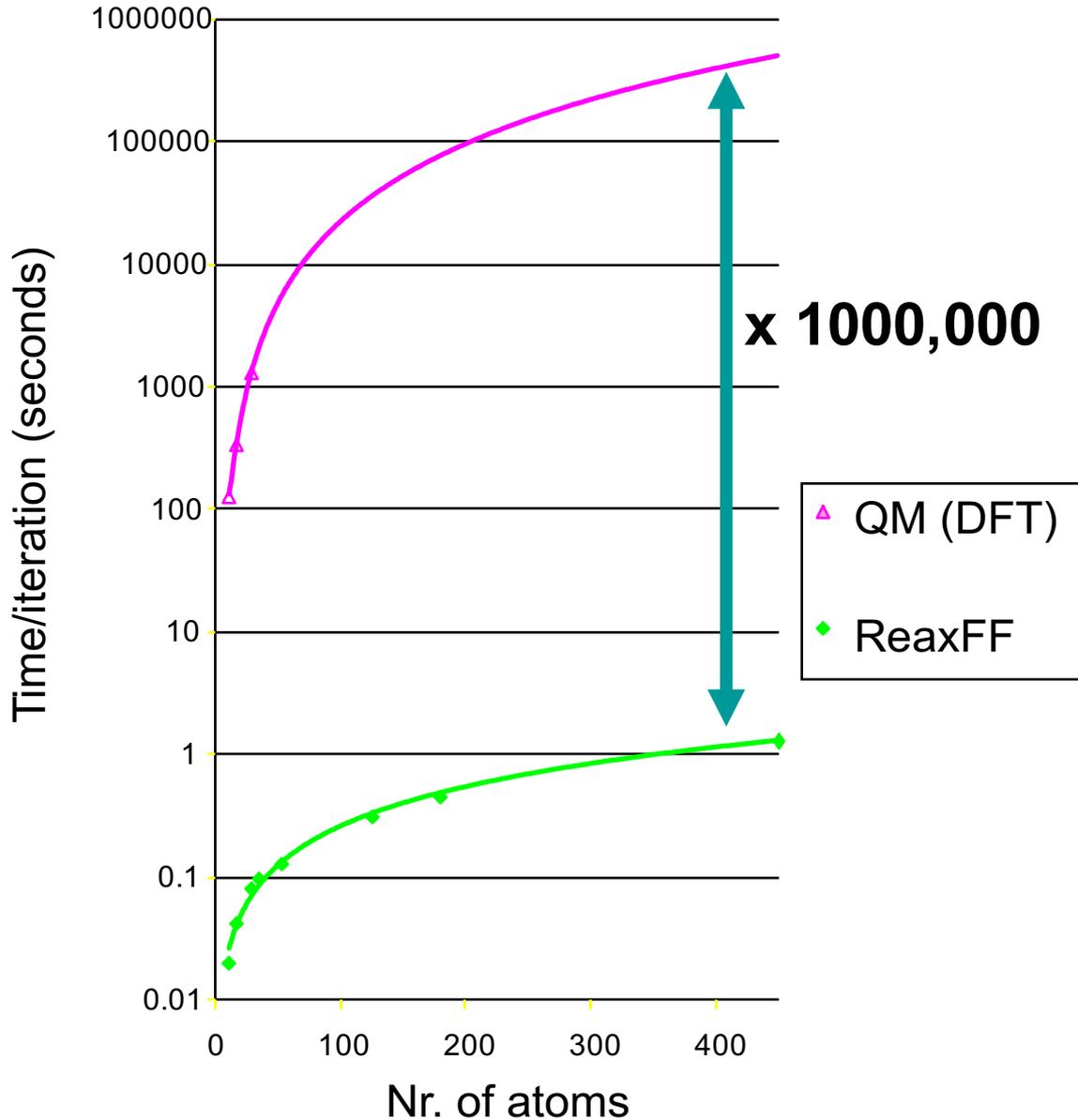


- Good reproduction of Mulliken charges (similar concepts)
- Combined with 1-2 Coulomb-interactions, this enables ReaxFF to simulate polarization effects on local chemistry
- EEM/Qeq methods work well around equilibrium; incorrect description of charge flow at high compression and dissociation (Chen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

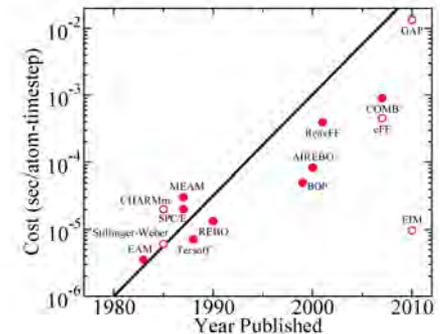
## General rules for ReaxFF

- 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

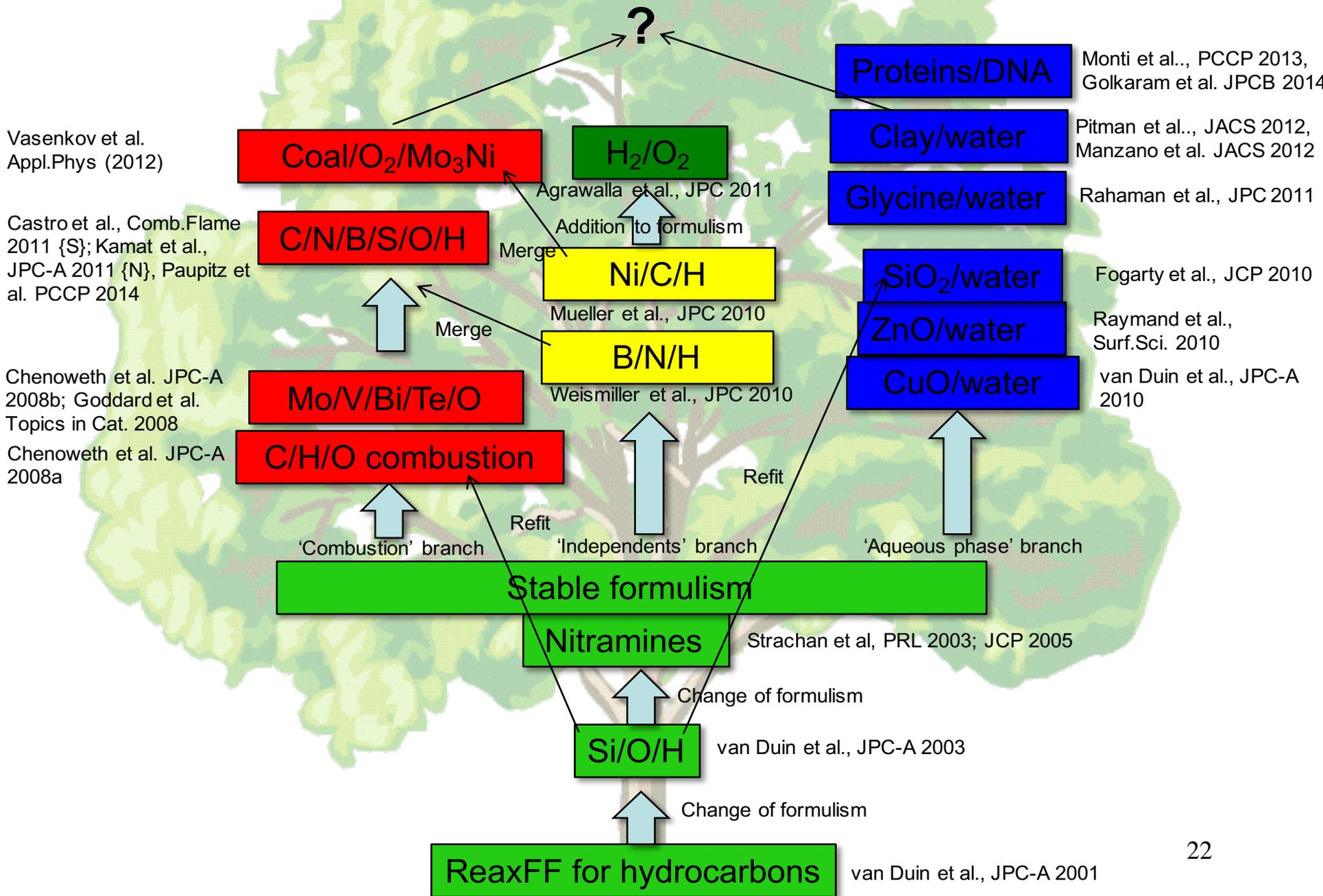


- ReaxFF allows for reactive MD-simulations on systems containing more than 1000 atoms
- ReaxFF is 10-50 times slower than non-reactive force fields
- Better scaling than QM-methods ( $N \log N$  for ReaxFF,  $N^3$  (at best) for QM)



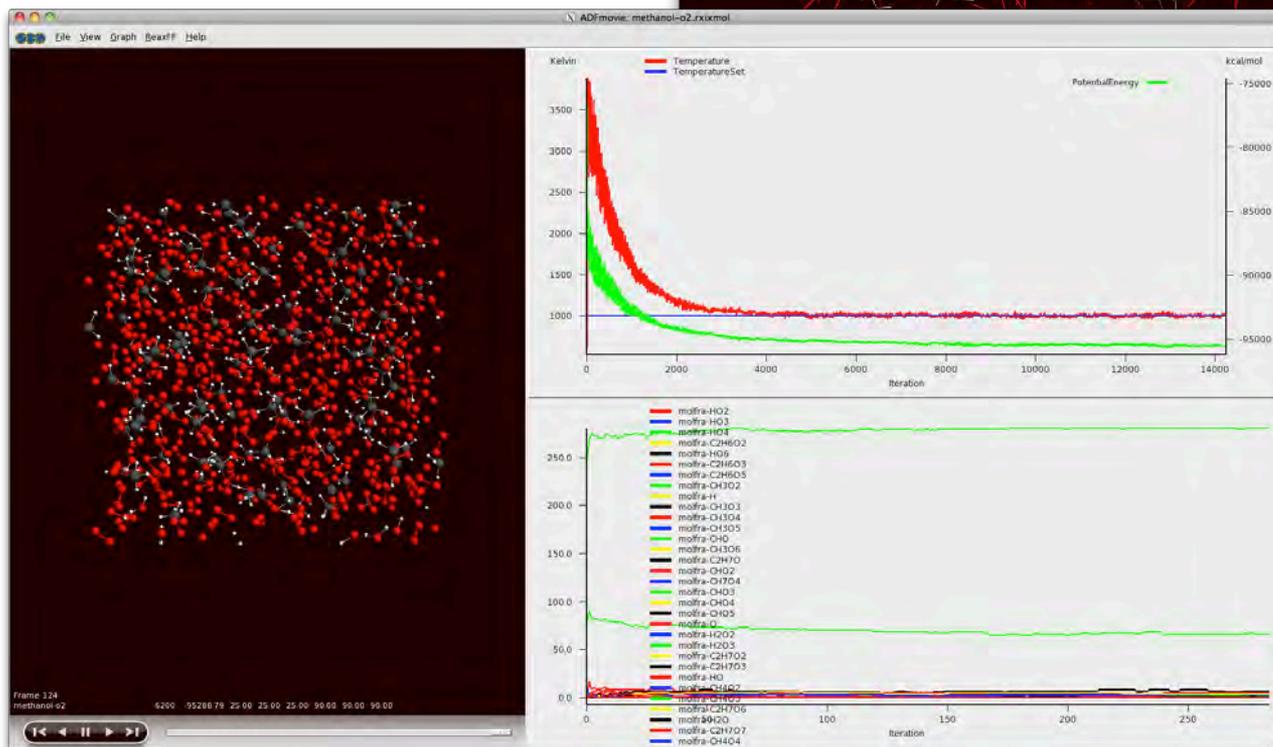
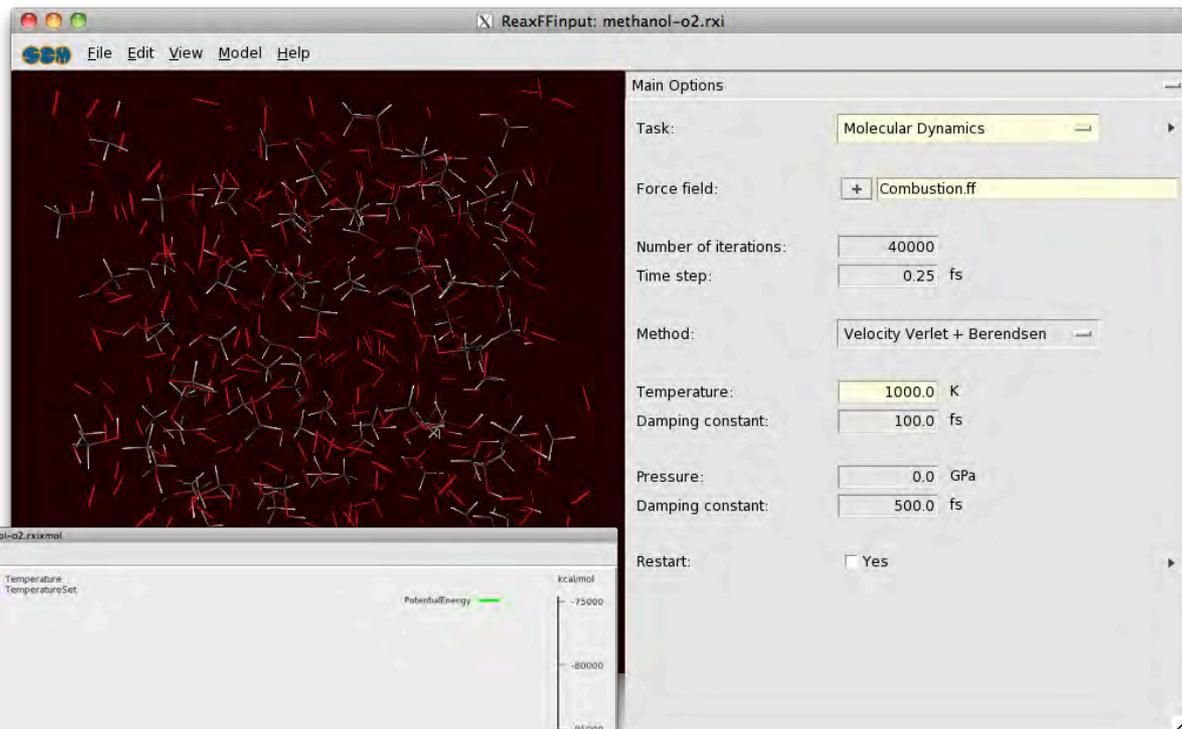


# ReaxFF development tree: towards complex materials



# ReaxFF integration into ADF/BAND graphical user interface

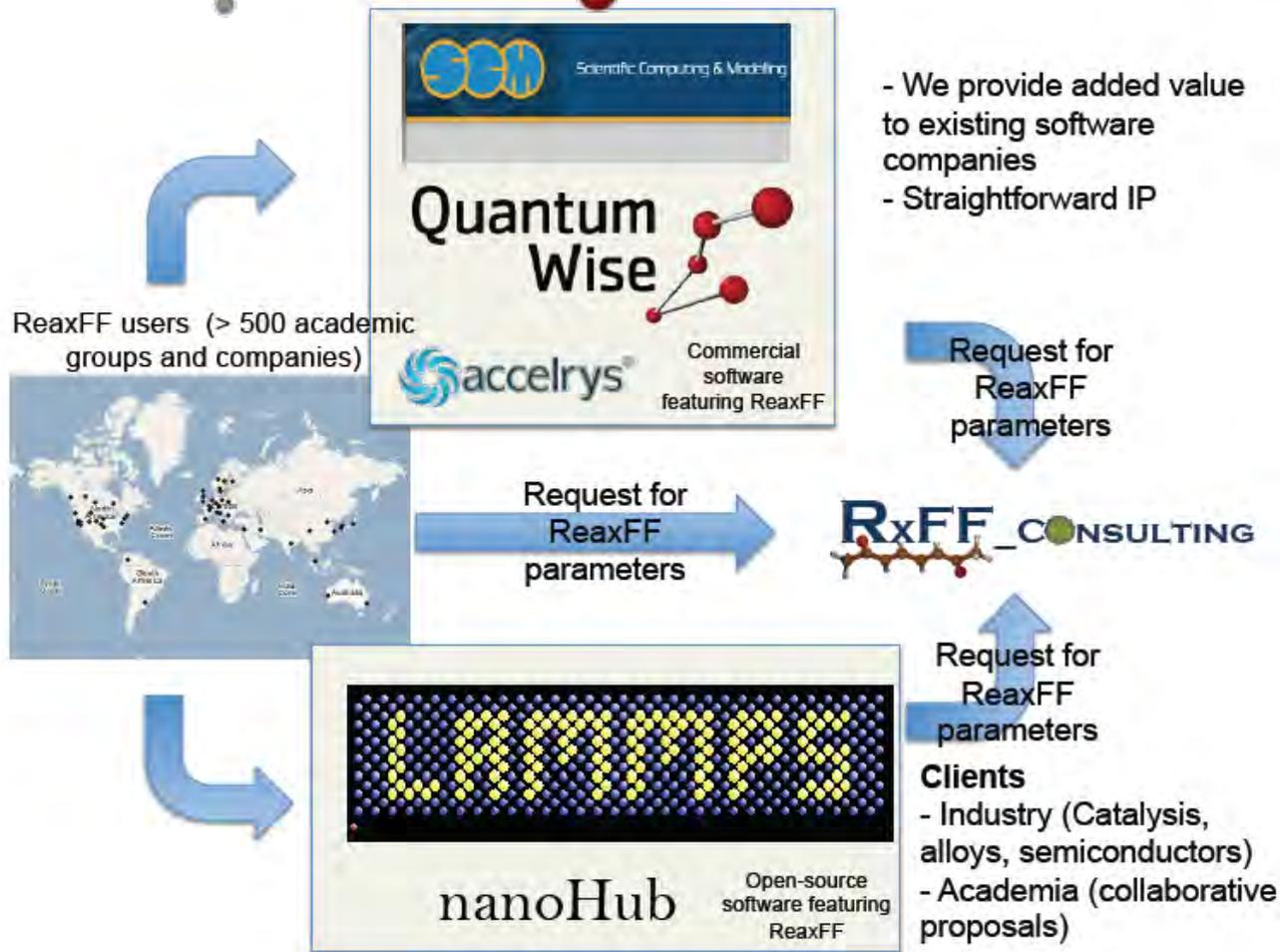
- Collaboration with SCM.
- Professional software support team.
- Parallel version.
- Direct integration of state-of-the-art DFT/FF/TB codes.



## Integration team:

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

# RxFF\_CONSULTING



- We provide added value to existing software companies
- Straightforward IP

Dr. Adri van Duin  
CTO

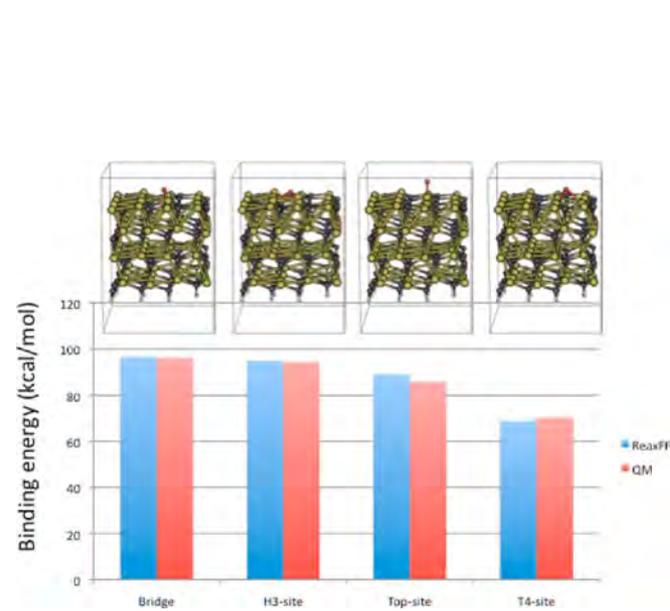
Dr. Diana van Duin  
CEO

- Request for ReaxFF parameters
- Clients**
  - Industry (Catalysis, alloys, semiconductors)
  - Academia (collaborative proposals)

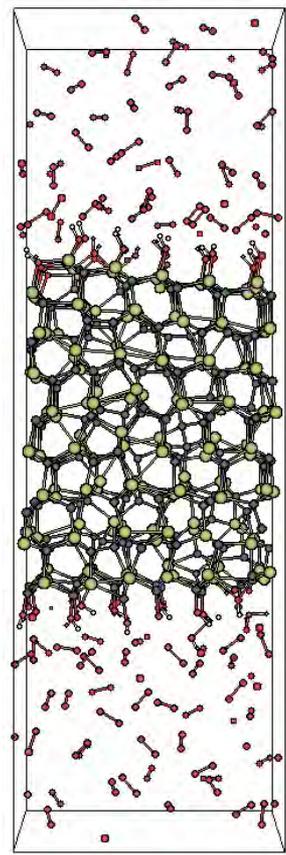
- Founded Sept. 2013
- 9 ongoing projects, including DoD SBIR Phase II
- Industry, academia clients

# A typical reactive force field project outline

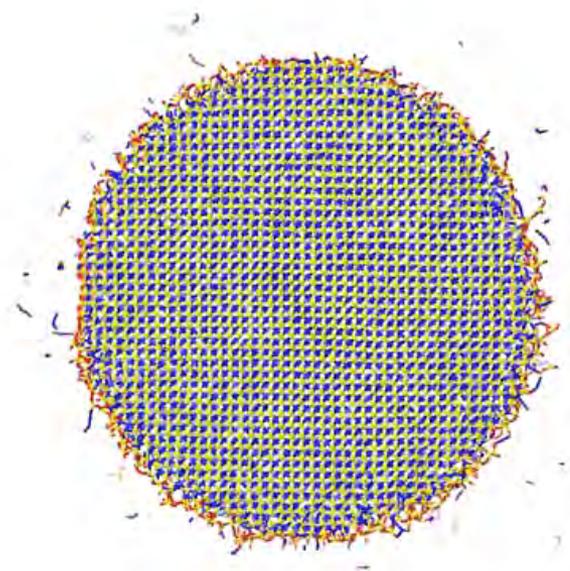
Development and application of ReaxFF to silicon carbide oxidation



- Train force field against QM-data (Newsome et al. JPC-C 116, 16111, 2012)

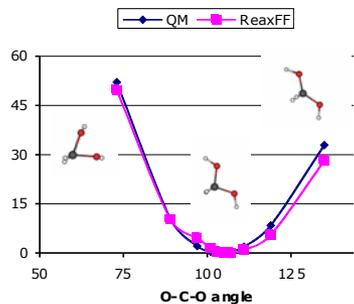


- Single-processor simulations (<4000 atoms) (Newsome et al. JPC-C 117, 5014, 2013)

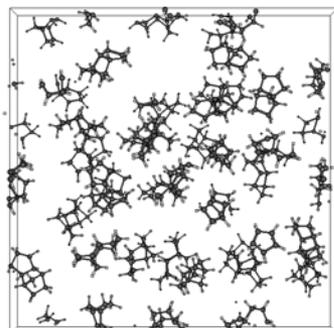


- Massively parallel, large scale (>> 1,000,000 atoms) reactive MD (Nomura et al. Scientific Reports 2016)

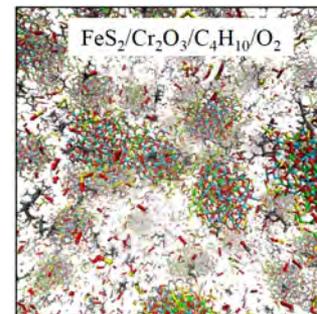
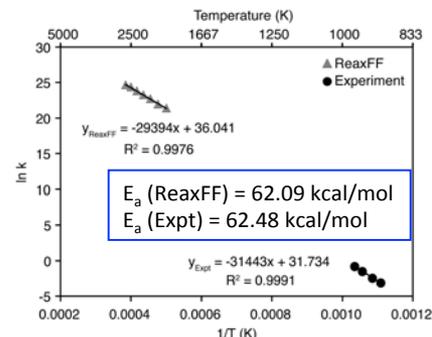
# Combustion/catalysis



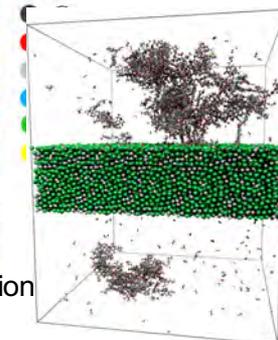
Angle distortion in  $\text{CH}_2(\text{OH})_2$   
(Chenoweth et al. JPC-A 2008)



JP-10 pyrolysis – comparison with experiment  
(Chenoweth et al. JPC-A 2008)

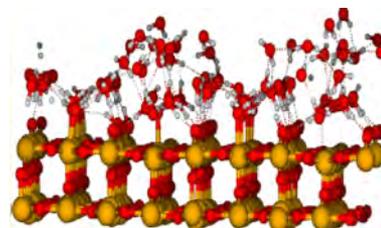


Butane catalytic conversion  
on pyrite/chromia  
(Shin et al. ACS Catalysis  
2015)

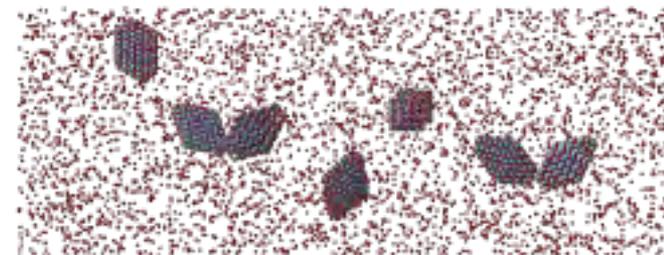


Coal combustion on a  
MoNi alloy surface  
(Vasenkov et al. JAP  
2012)

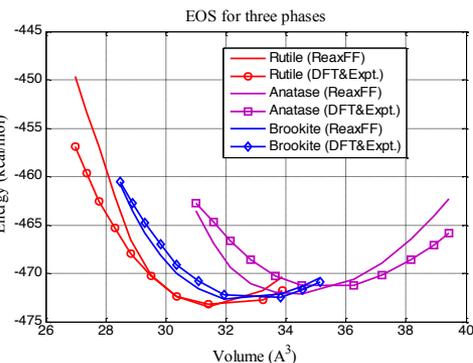
# Crystal growth



Water structure and reactivity on  $\text{TiO}_2$ -surfaces  
(Raju et al. JPC-C 2013)

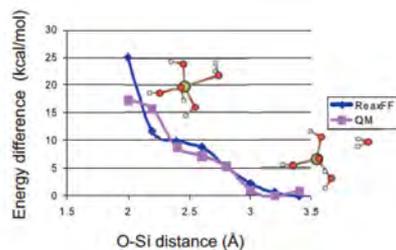


Oriented crystal growth of  $\text{TiO}_2$  NPs in water  
(Raju et al. Nano Letters 2014)

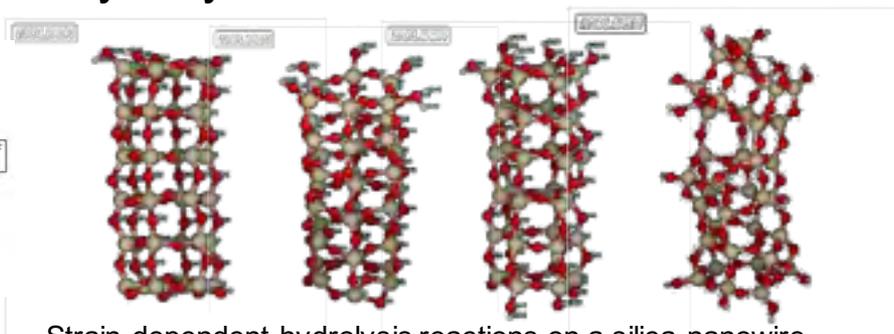


$\text{TiO}_2$  equations of state  
(Kim et al. Langmuir 2013)

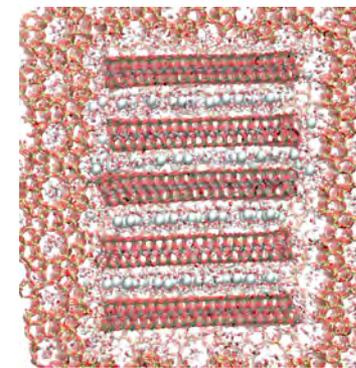
# Hydrolysis reactions on mineral surfaces



Water approach to silanol  
(Fogarty et al. JCP 2010)



Strain-dependent hydrolysis reactions on a silica nanowire  
(Yeon et al. JPC-C 2016)

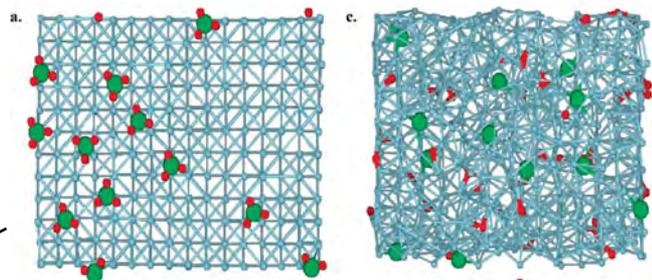


Water diffusion in clay/zeolite interfaces  
(Pitman et al. JACS 2012)



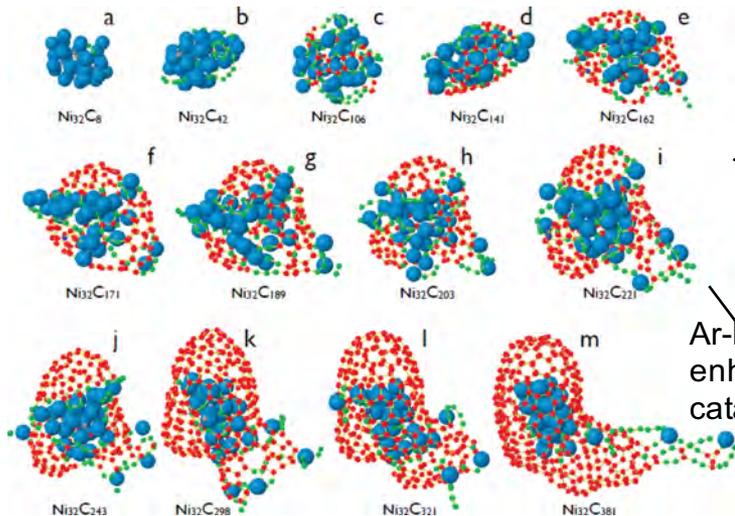
# Applications to catalytic carbon-growth on Ni-surfaces

Collaborations with Jonathan Mueller (Caltech, currently U.Ulm) and Erik Neyts (U. Antwerp)

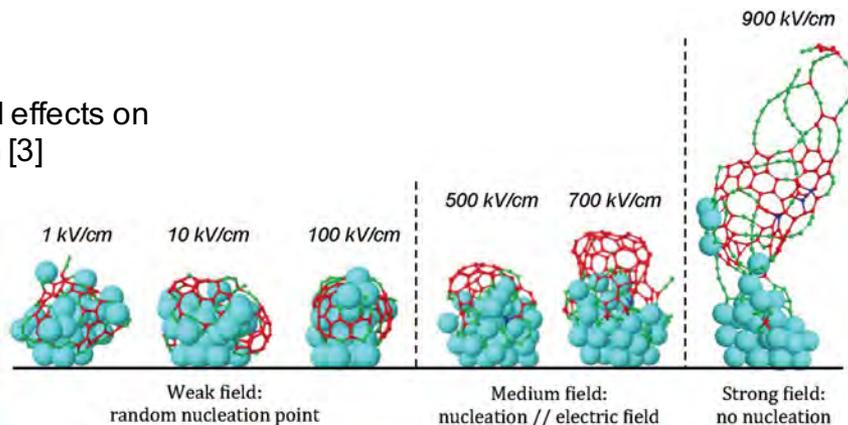


Development of Ni/hydrocarbon ReaxFF [1]

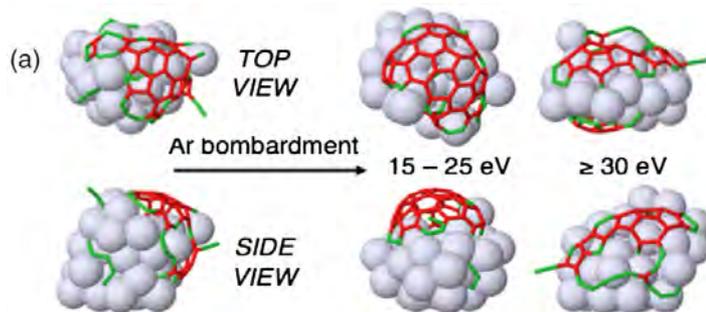
Integration of force-biased Monte Carlo [2]



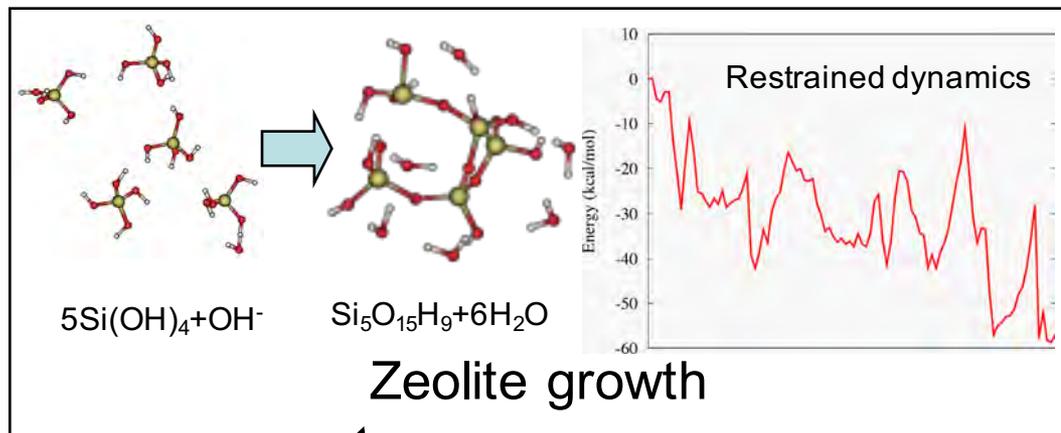
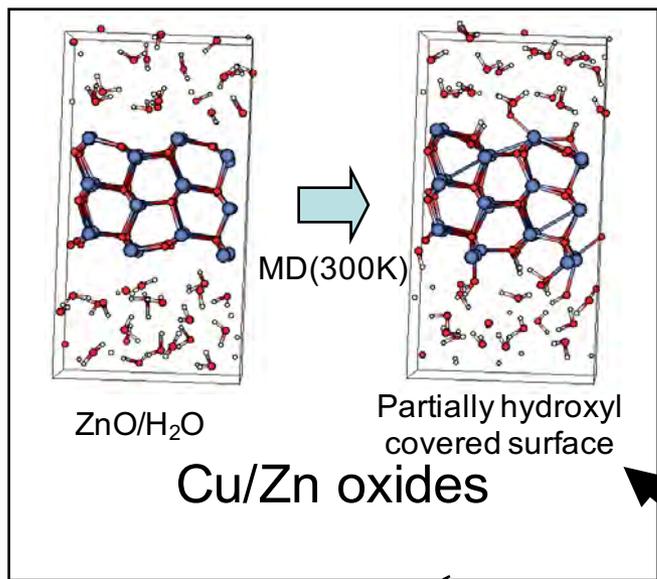
Electric field effects on CNT-growth [3]



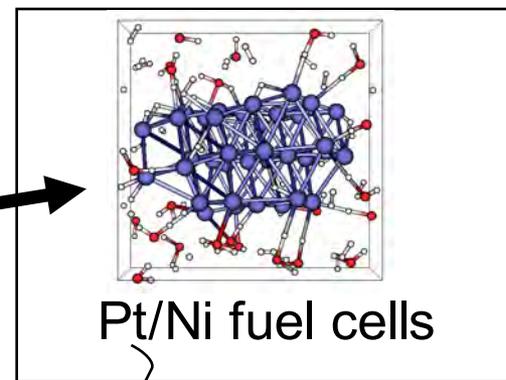
Ar-bombardment enhanced surface catalysis [4]



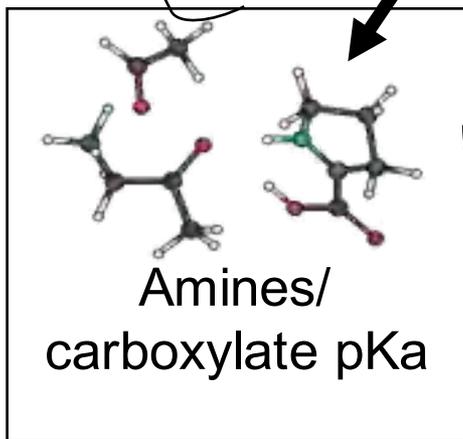
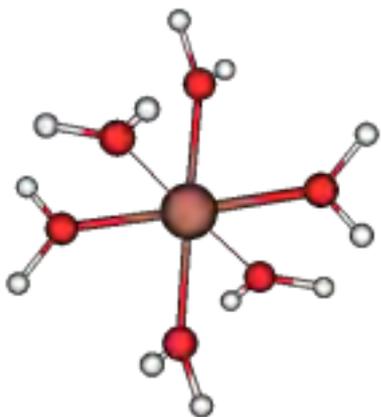
- (1) Mueller, J. E.; van Duin, A. C. T.; Goddard, W. A., III. *Journal of Physical Chemistry C* 2010, 114, 4939.
- (2) Neyts, E. C.; Shibuta, Y.; van Duin, A. C. T.; Bogaerts, A. *ACS Nano* 2010, 4, 6665.
- (3) Neyts, E. C.; van Duin, A. C. T.; Bogaerts, A. *Journal of the American Chemical Society* 2012, 134, 1256.
- (4) Neyts, E. C.; Ostrikov, K.; Han, Z. J.; Kumar, S.; van Duin, A. C. T.; Bogaerts, A. *Physical Review Letters* 2013, 110, 065501.



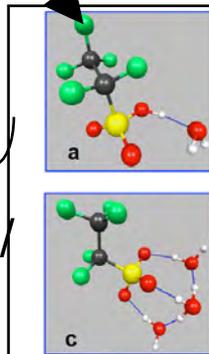
**ReaxFF for water**



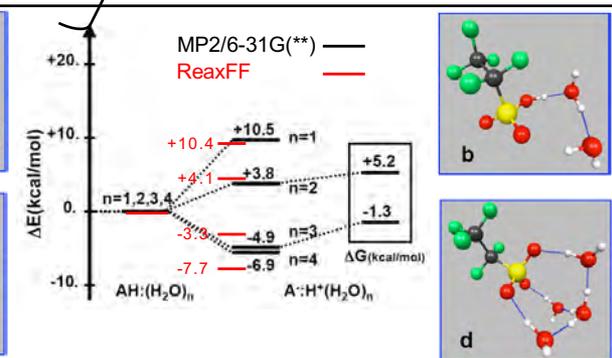
**Dendrimers/metal cations**



**Enzymes/ DNA/ organic catalysis**

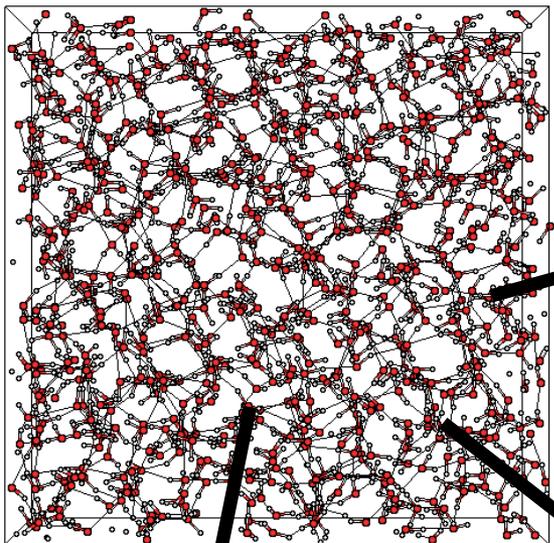


**Nafion fuel cell**

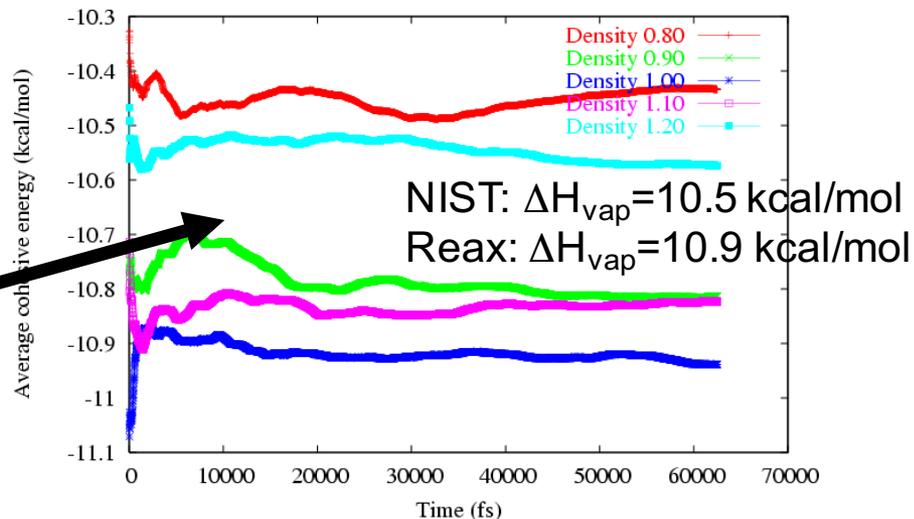


# Molecular dynamics tests of ReaxFF for bulk water [1]

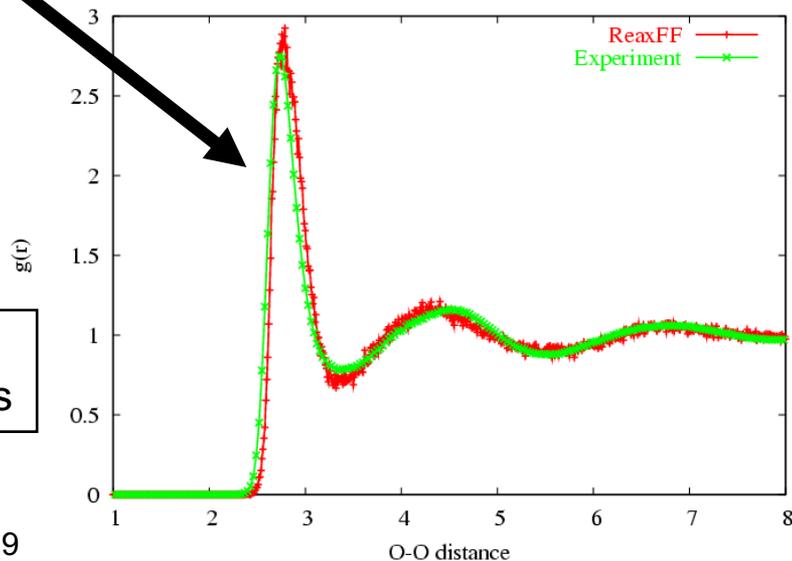
800 water box



Density,  
cohesive  
energy

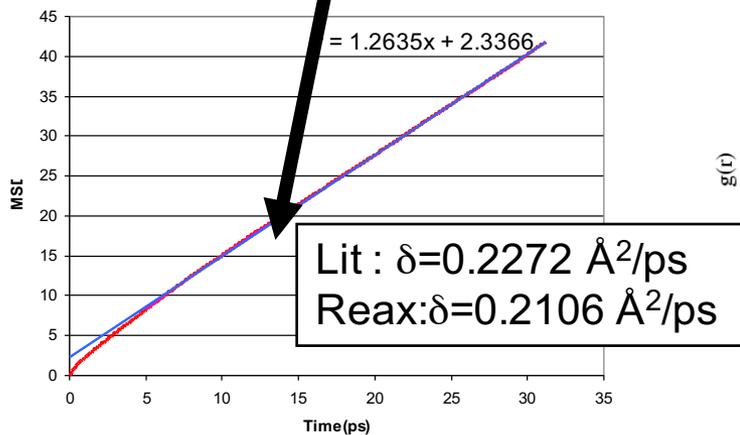


Radial  
distribution



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

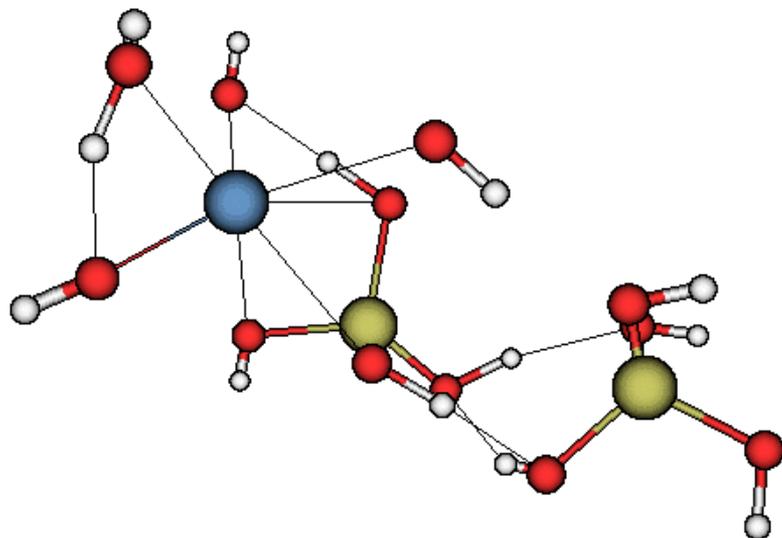
Diffusion constant



Eisenberg and Kauzman, Oxford Univ. Press 1969

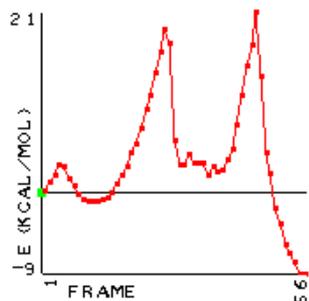
[1] van Duin, A. C. T., Zou, C., Joshi, K., Bryantsev, V. S., and Goddard, W. A., 2013. A ReaxFF reactive force field for proton transfer reactions in bulk water and its applications to heterogeneous catalysis. Royal Society of Chemistry, Cambridge.

# Water/silica chemistry – influence of electrolytes



Si(OH)<sub>4</sub> dimerization catalyzed by a Ca(OH)<sub>2</sub>.2H<sub>2</sub>O complex

- Ca-ion assists by coordinating to the silanol-group, facilitating proton transfer to a hydroxyl coordinated to the Ca-cation
- Barrier with Ca: 21 kcal/mol; without Ca: 28 kcal/mol (DFT/B3LYP/6-311G\*\* [1])
- Ca/O/H parameters from Manzano et al., Langmuir 2012 [2]



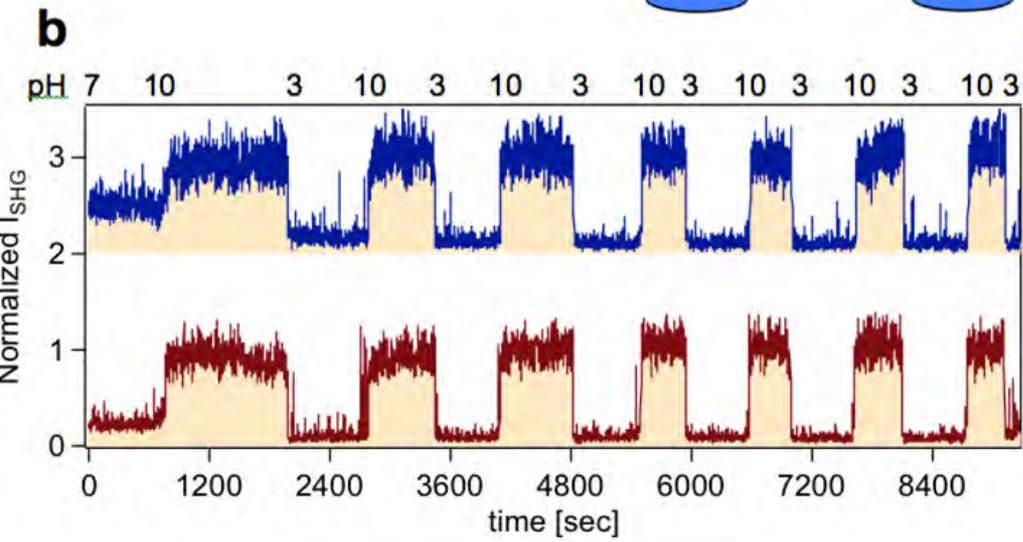
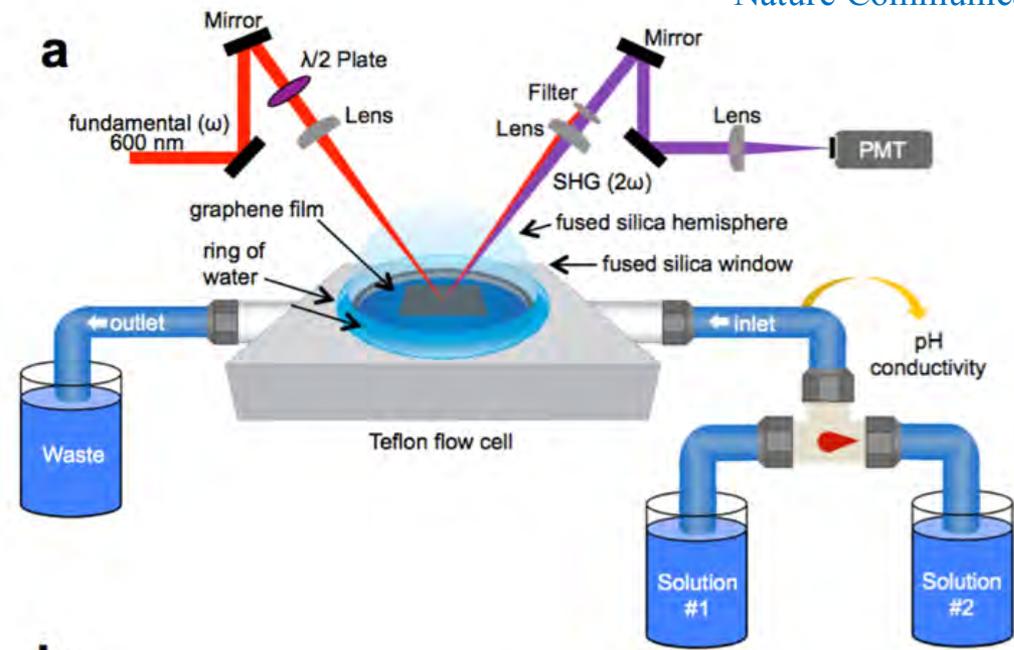
MD/NVT-simulation at T=25K with sliding restraint to drive reaction  
5000 iterations  
CPU-time (this laptop) 35 seconds

[1] Criscenti and Kubicki, J.Phys.Chem.A 2006

[2] Manzano, Pellenq, Ulm, Buehler and van Duin, Langmuir 2012

# Aqueous Proton Transfer Across Single Layer Graphene

Jennifer Achtyl, Raymond Unocic, Lijun Xu, Yu Cai, Muralikrishna Raju, Wei Zhang, Robert L. Sacci, Ivan V. Vlasiouk, Pasquale F. Fulvio, Ganesh, P. David Wesolowski, Sheng Dai, Adri van Duin, Matthew Neurock, Franz Geiger, Nature Communications 2015.



- Does single-layer graphene act as a perfect barrier to proton exchange ?
- To test this hypothesis,
  - Single layer graphene is placed between an aqueous phase and the surface of an amphoteric oxide
  - Aqueous phase is cycled between acidic and basic pH
  - Cycling the pH changes the relative concentration of species on the silica surface ( $\text{SiOH}$ ,  $\text{SiOH}_2^+$ ,  $\text{SiO}^-$ )
  - Second Harmonic Generation (SHG) signals depend on the relative concentration of these species



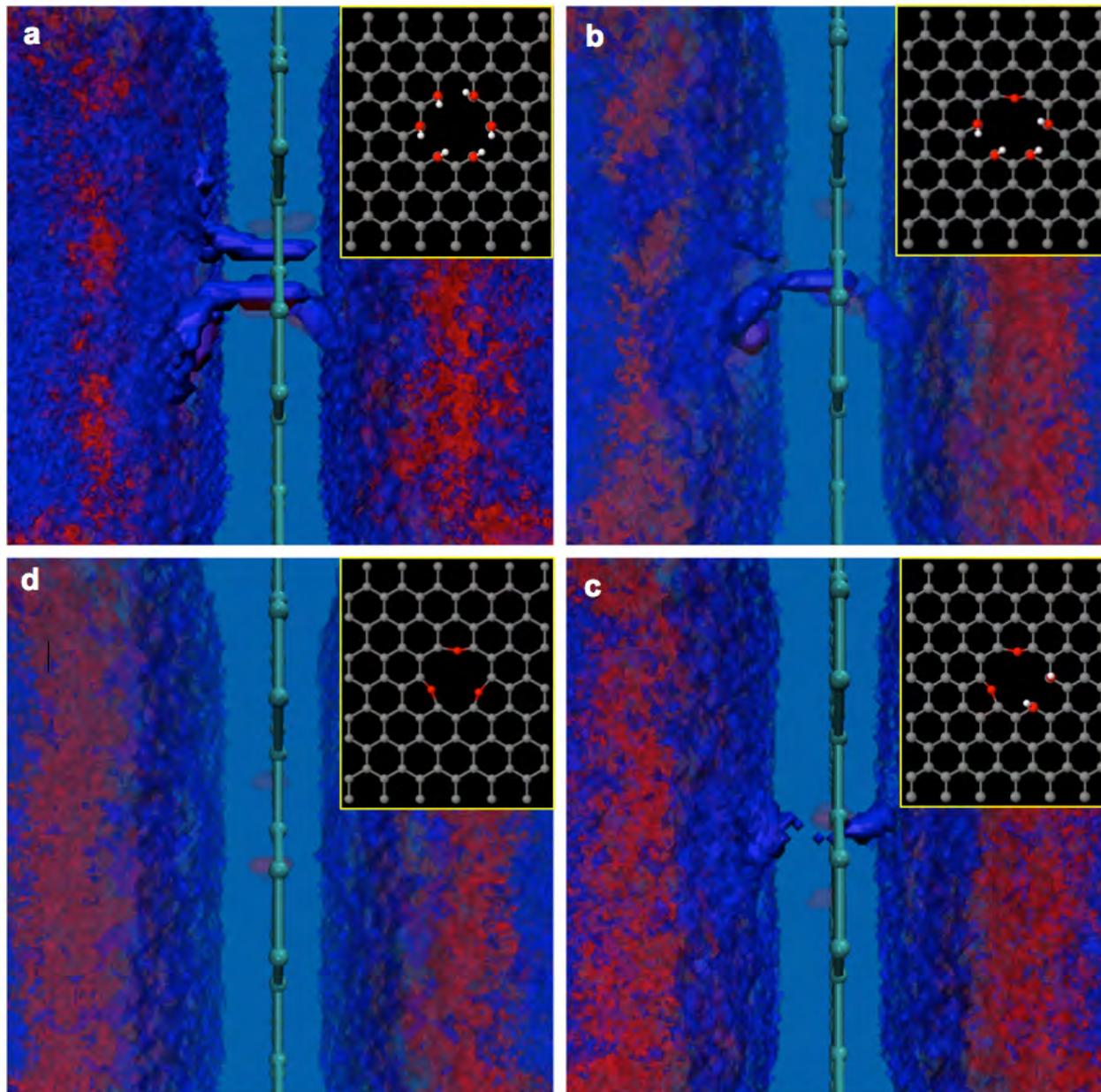
# Comparison of DFT and ReaxFF-calculated activation barriers

## DFT and ReaxFF-calculated activation barriers for proton transfer through different vacancy sites on graphene in water

Graphene Surface	Bottom Layer	Defect Termination	Activation Barrier <i>DFT</i> *	Activation Barrier <i>ReaxFF</i> *
No vacancy	Water	No termination	3.9 eV	> 5 eV
1V	Water	No termination	> 2.0 eV	3.54 eV
4V	Water	No termination	0.25 eV	0.22 eV
4V	Water	3O ether capped	1.8 eV	1.7 eV
4V	Water	6OH hydroxyl capped	0.68 eV	0.61 eV
4V	Water + SiO <sub>2</sub>	3O ether capped	2.5 eV	2.53 eV
4V	Water + SiO <sub>2</sub>	6OH hydroxyl capped	0.7 eV	0.75 eV

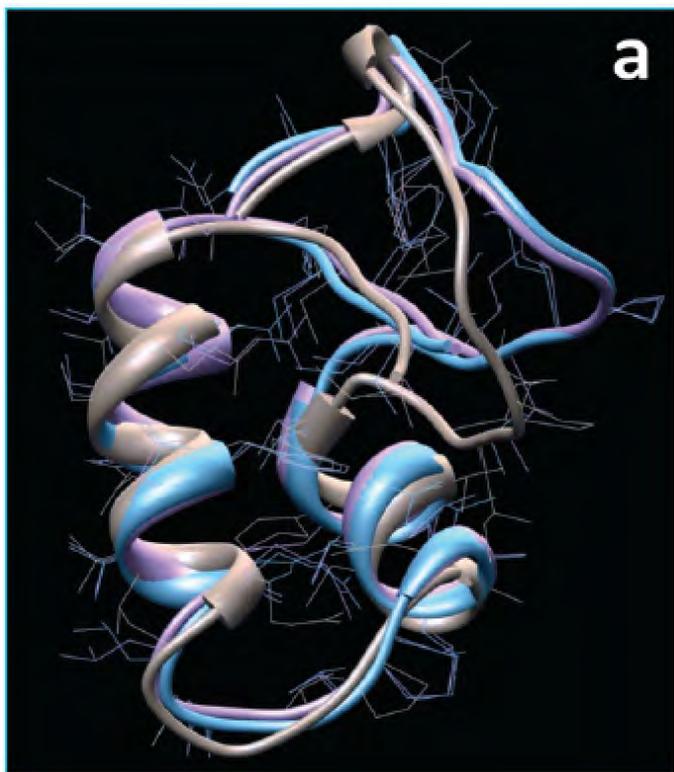
- Excellent agreement between ReaxFF and DFT- especially for the important, low-barrier events.
- ReaxFF allows us to study the dynamics of proton transfer in large (>> 1000 atoms), long-time (>> 1 nanoseconds) MD-simulations,

# Proton transfer channel formation from ReaxFF MD simulations at 300 K

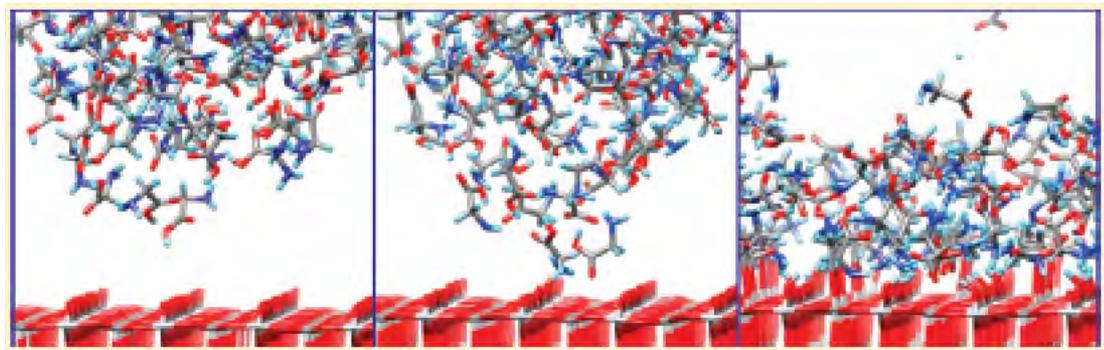


- The protons are transferred via proton shuttling following a Grotthuss mechanism along a network of O-H-O-H bonds that make up the proton relay conduit.
- ReaxFF simulations clearly show the formation of a proton transfer channel through the six hydroxyl terminated 4V site (Fig.a).
- **This channel thins when the three pairs of OH groups terminating the defect site are replaced, one by one, with oxygen atoms (Fig. b, c).**
- **The proton transfer channel is fully disrupted when the defect site is terminated by three oxygen atoms (Fig. d).**

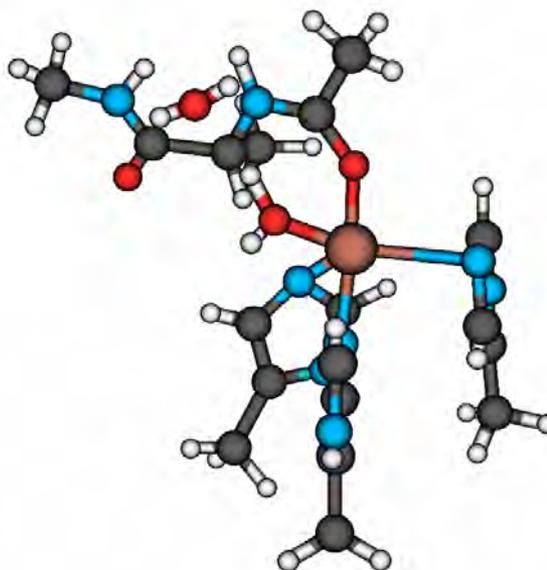
# New direction: biomaterials and their interface chemistry



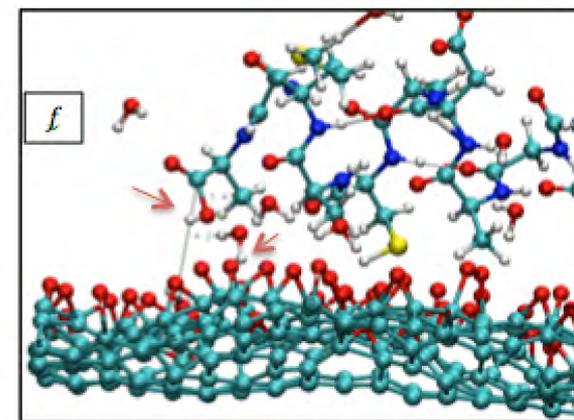
AMBER(pink), ReaxFF(tan) and native structure (cyan) of Cambin in water (Monti, Shin, van Duin et al. Phys.Chem.Chem.Phys 2013, **15**, 15062)



Reactions of a glycine droplet on a titania surface (Monti, van Duin, Kim and Barone, J.Phys.Chem.C 2012, **116**, 5141)



Simulation of copper-complex catalyzed peptide cleavage

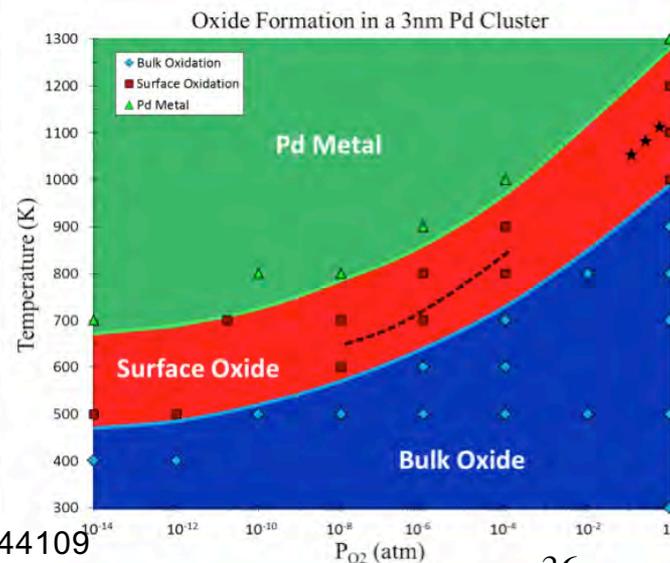
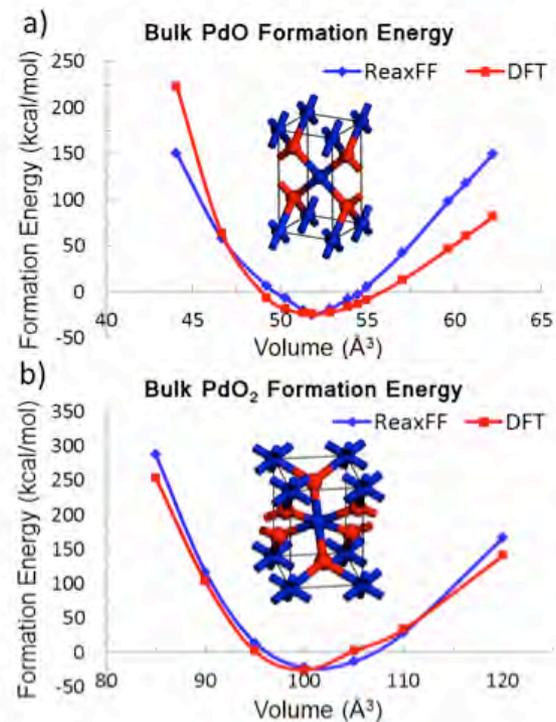
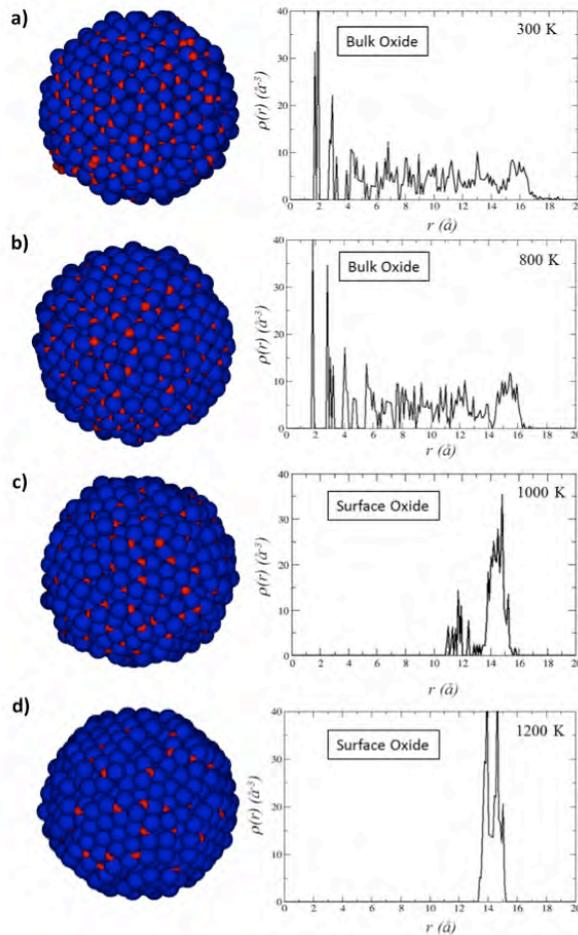


Simulation of proton-transfer induced de-helicalization on a polypeptide/graphene oxide interface (Golkaram, Shin and van Duin, manuscript in progress)

# Hybrid Grand Canonical Monte Carlo/MD ReaxFF [1]

With Thomas Senftle and Michael Janik

- Enables prediction of thermodynamic end states at various P/T conditions
- Application to PdO<sub>x</sub> shows high-T reduction, in good agreement with experiment [2,3]
- Hybrid GCMC/MD allows crystal morphology change during oxidation/reduction
- Highly transferable tool



[1] Senftle, Janik, Meyer and van Duin, Journal of Chemical Physics **2013**, 139, 044109

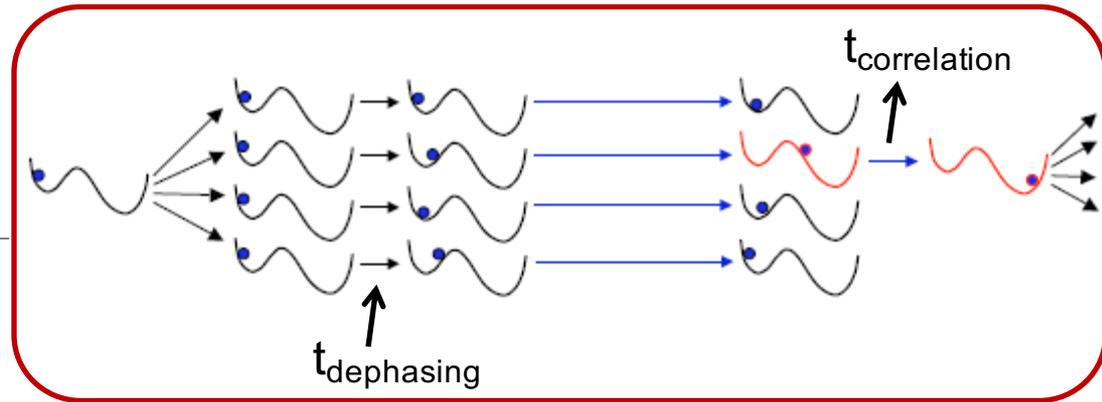
[2] Ketteler, G.; Ogletree, D. F.; Bluhm, H.; Liu, H. J.; Hebenstreit, E. L. D.; Salmeron, M. *J. Am. Chem. Soc.* **2005**, 127, 38269.

[3] Zhang, H.; Gromek, J.; Fernando, G.; Marcus, H.; Boorse, S. Journal of Phase Equilibria and Diffusion **2002**, 23, 246.

# Parallel Replica Dynamics with ReaxFF in LAMMPS (Kaushik Joshi & Sumathy Raman(EMRE))

- PRD<sup>1</sup> parallelizes rare event simulation in time domain and accelerate time scale of MD

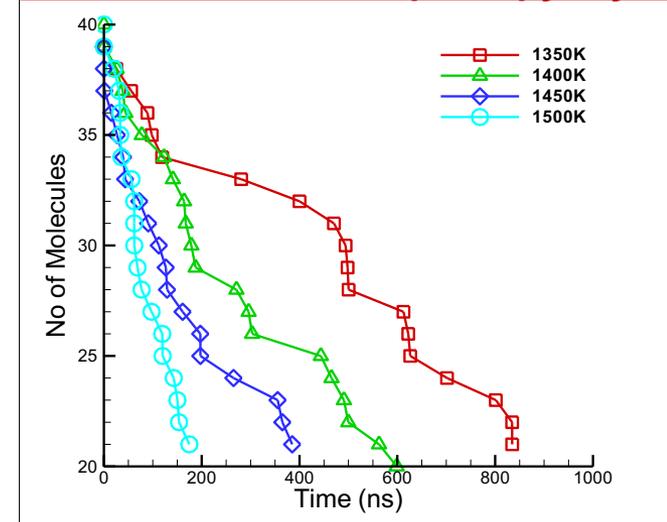
- Infrequent events
- Transitions can be detected
- Exponential distribution of first-escape times
- Correlation time known



- PRD is coupled with REAXFF [2] in by implementing a connectivity-based event detection

	PRD	Experiment <sup>7</sup>
$E_a$ (kcal/mol)	50.01	54
Pre exponential factor ,A	$7.17 \times 10^{13}$	$6.3 \times 10^{11}$

**PRD Results on n-heptene pyrolysis**

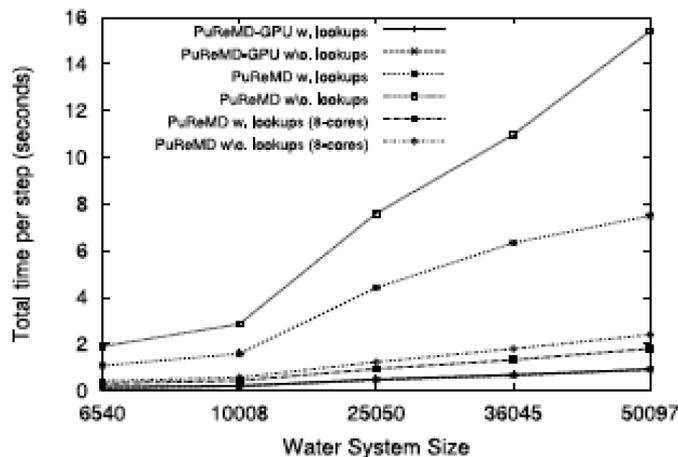


<sup>1</sup>Phys. Rev. B, 57, R13985 (1998); <sup>7</sup> Blades A.T., Sandhu H.S. (1971) Int. J. Kin., 3 187-193

<sup>2</sup>: Joshi, Raman and van Duin, J.Phys.Chem.Letters 4, 3792 (2013)

# ReaxFF/GPU developments

- ReaxFF/GPU published by Zheng, M., Li, X., and Guo, L., 2013. Algorithms of GPU-enabled reactive force field (ReaxFF) molecular dynamic. Journal of Molecular Graphics and Modelling 41. Single precision ?
- Ananth Grama-group has finished an initial ReaxFF/GPU version, based on C++/ReaxFF version integrated in LAMMPS. Double precision, gcc 4.5.4, CUDA 5.0 (Kylasa, Aktulga and Grama, J.Comp.Chem. 2014, 272, 343)
- Purdue/GPU/ReaxFF looks promising – 4 times faster then best current ReaxFF method for 2000 atoms; looks even better for larger systems (5000-10,000 atoms).
- Needs further development (memory management, parallel GPU)



# Improved charge calculation: ACKS2

## Condensed form for the 'electronic energy'

$$E_{\text{EEM}} = \left( \sum_A \chi_A q_A + \frac{1}{2} \eta_A q_A^2 \right) + \left( \frac{1}{2} \sum_{A,B \neq A} \frac{q_A q_B}{|\mathbf{r}_A - \mathbf{r}_B|} \right)$$

Variables:  $q_i$

Parameters:  $\chi_i, \eta_i, \bar{r}_i$

## Charges minimize $E_{\text{EEM}}$ (with total charge constraint)

$$\frac{\partial E_{\text{EEM}}}{\partial q_A} = \sum_A \left( \chi_A + \eta_A q_A + \sum_{B \neq A} \frac{q_B}{|\mathbf{r}_A - \mathbf{r}_B|} \right) = \chi_{\text{mol}}$$

## EEM equations in block matrix notation

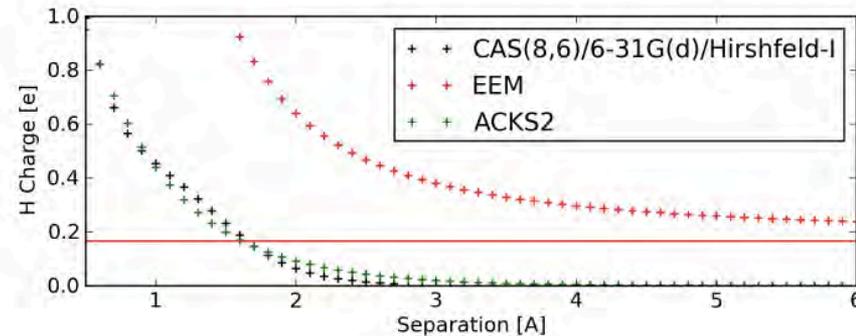
$$- \begin{bmatrix} \eta & -d \\ -d^T & 0 \end{bmatrix} \begin{bmatrix} q \\ \chi_{\text{mol}} \end{bmatrix} = \begin{bmatrix} \chi \\ q_{\text{tot}} \end{bmatrix}$$

## ACKS2 equations in block matrix notation

$$- \begin{bmatrix} \eta & -d & -I & 0 \\ -d^T & 0 & 0 & 0 \\ -I & 0 & X_S & -d \\ 0 & 0 & -d^T & 0 \end{bmatrix} \begin{bmatrix} \Delta \\ \mu_{\text{mol}} \\ W \\ \lambda_W \end{bmatrix} = \begin{bmatrix} \mu \\ 0 \\ 0 \\ 0 \end{bmatrix}$$

In collaboration with Toon Verstraelen  
(U. Gent)

## Charges on H during HF-dissociation

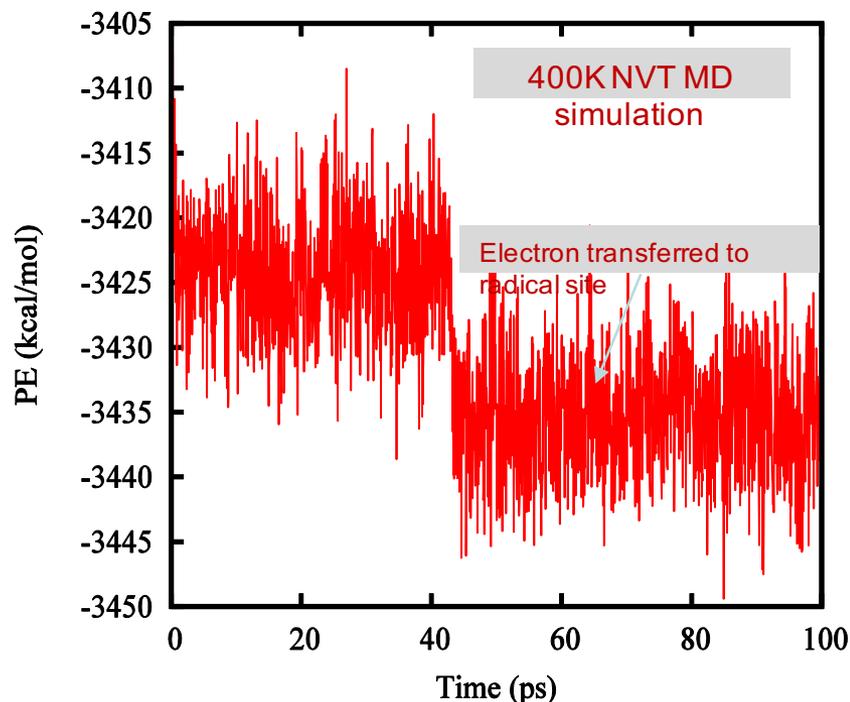


- EEM gives non-zero charges after bond dissociation
- ACKS2 enforces integer charges
- ACKS2 solves polarization issues (EEM: metallic)

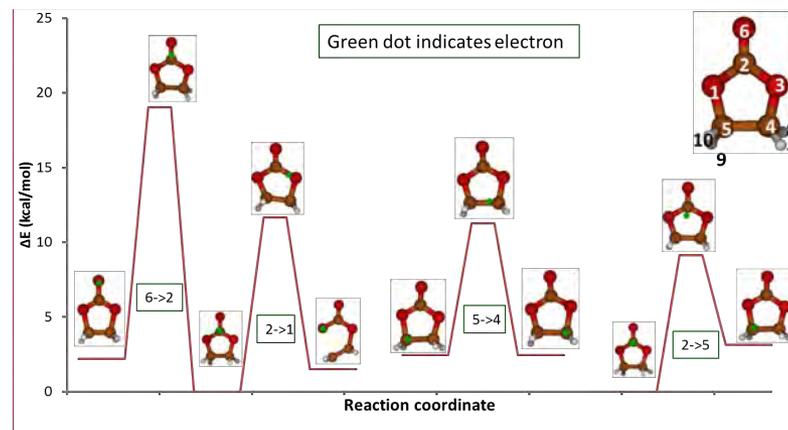
Verstraelen et al. JCP 2013<sup>39</sup>

# Inclusion of explicit electrons/holes ( e-ReaxFF )

Mahbub Islam and van Duin [1]



Electron migration across a  $sp^3$ -region to a radical site



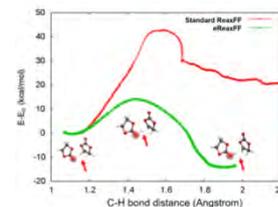
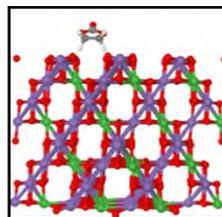
## Barriers for intramolecular electron transport in EC

- e-ReaxFF integrates aspects of the eFF-reactive force field [2] into the ReaxFF method
- Enables simulations including explicit electron transfer – relevant to battery interface chemistry
- Fully transferable to existing ReaxFF descriptions

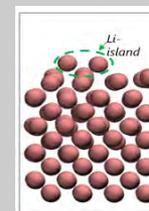
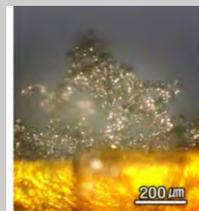
[1] Islam and van Duin, JCTC 2016 (online)  
[2] Su, J. T. and Goddard, W. A., 2007 Phys. Rev. Lett. 99, 185003.

# e-ReaxFF/ACKS2 : Ongoing and Future Work

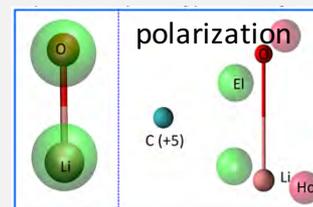
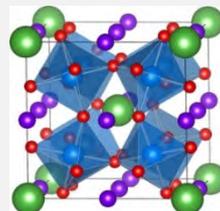
Cathode-electrolyte interface



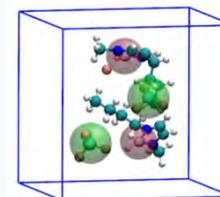
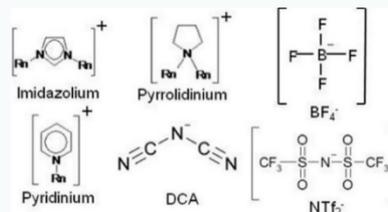
Li-dendrite growth



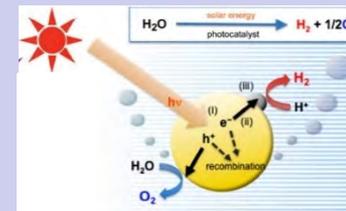
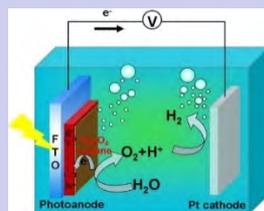
Piezo/Ferro electric materials



Ionic liquid system



Water-splitting photovoltaic cell



# 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 ( $\gg 1000$  atoms) systems (single processor). ReaxFF has now been parallelized, allowing reactive simulations on  $\gg 1000,000$  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	Ib	IIIa	IVa	Va	VIa	VIIa	0		
1	H	He														He		
2	Li	Be														Ne		
3	Na	Mg	Al	Si	P	S	Cl	Ar								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															

 : not currently described by ReaxFF

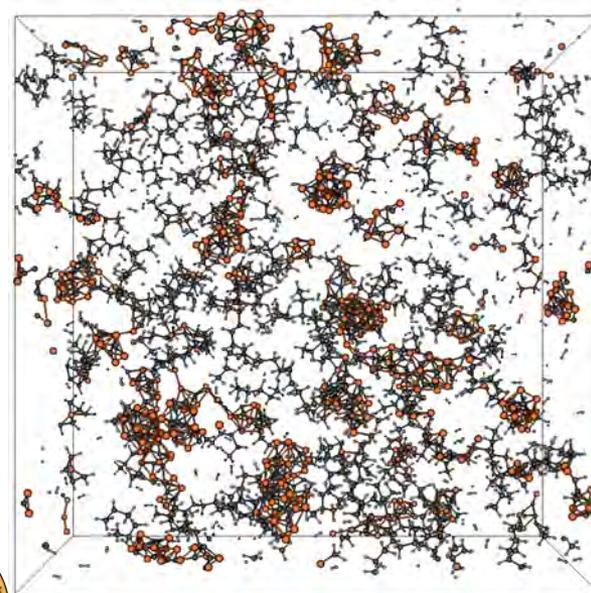
# Acknowledgments

## Collaborators:

- Jonathan Mathews, Jim Kubicki, Deborah Levin, Rich Yetter and Mike Janik (Penn State)
- Kimberley Chenoweth, Vyacheslav Bryantsev and Bill Goddard (Caltech)
- Aidan Thompson (Sandia), Metin Aktulga (Michigan State), Ananth Grama (Purdue), SCM (Amsterdam)

Funding: - PSU/KISK startup grant #C000032472

- ARL/MSME
- NSF (TiO<sub>2</sub>/water, PdO/Ceria, Li/C)
- NETL/RUA (Fuel catalysis)
- AFOSR/MURI (O-resistant materials)
- DoE/EFRC FIRST-center
- Exxon (Software development, catalysis)
- British Royal Society (initial ReaxFF funding)



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

Websites: <http://www.engr.psu.edu/adri>  
<http://www.rxffconsulting.com>

Office: 240 Research East  
Phone: 814-863-6277  
E-mail: [acv13@psu.edu](mailto:acv13@psu.edu)



More information: