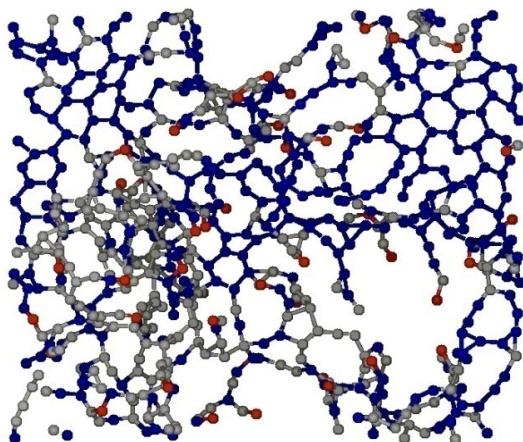


# Development and application of the ReaxFF reactive force field method

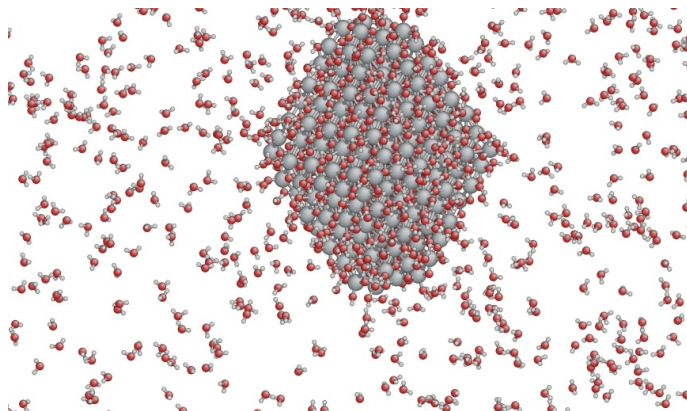
Adri van Duin, Murali Raju, Sriram Srinivasan, Jejoon Yeon, Sung-Yup Kim, Thomas Senftle and Kaushik Joshi

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

LAMMPS workshop, August  
2013

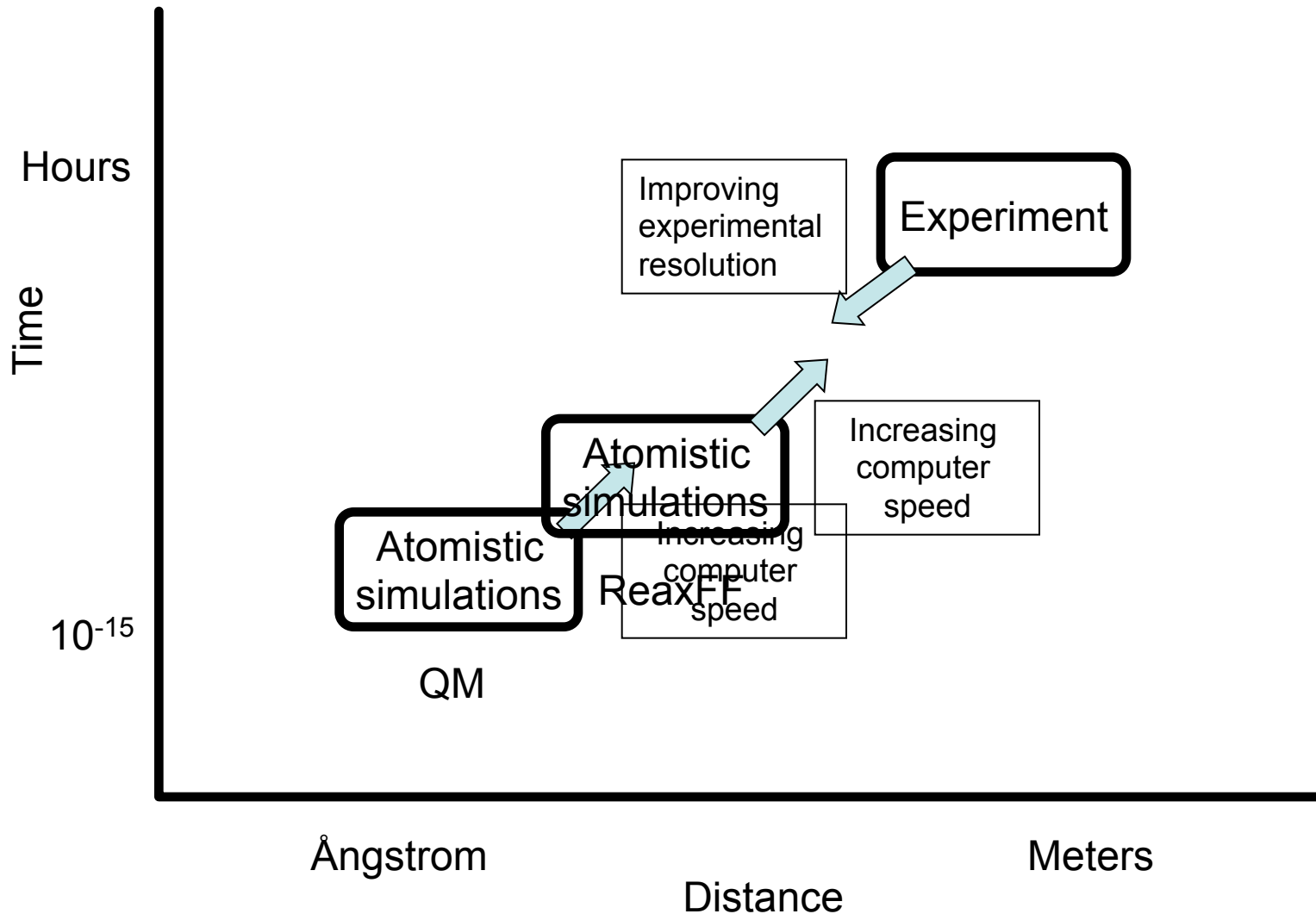


ReaxFF simulation of graphene breakup during oxidation (by Sriram Srinivasan; Srinivasan et al. JPC-A 2011)

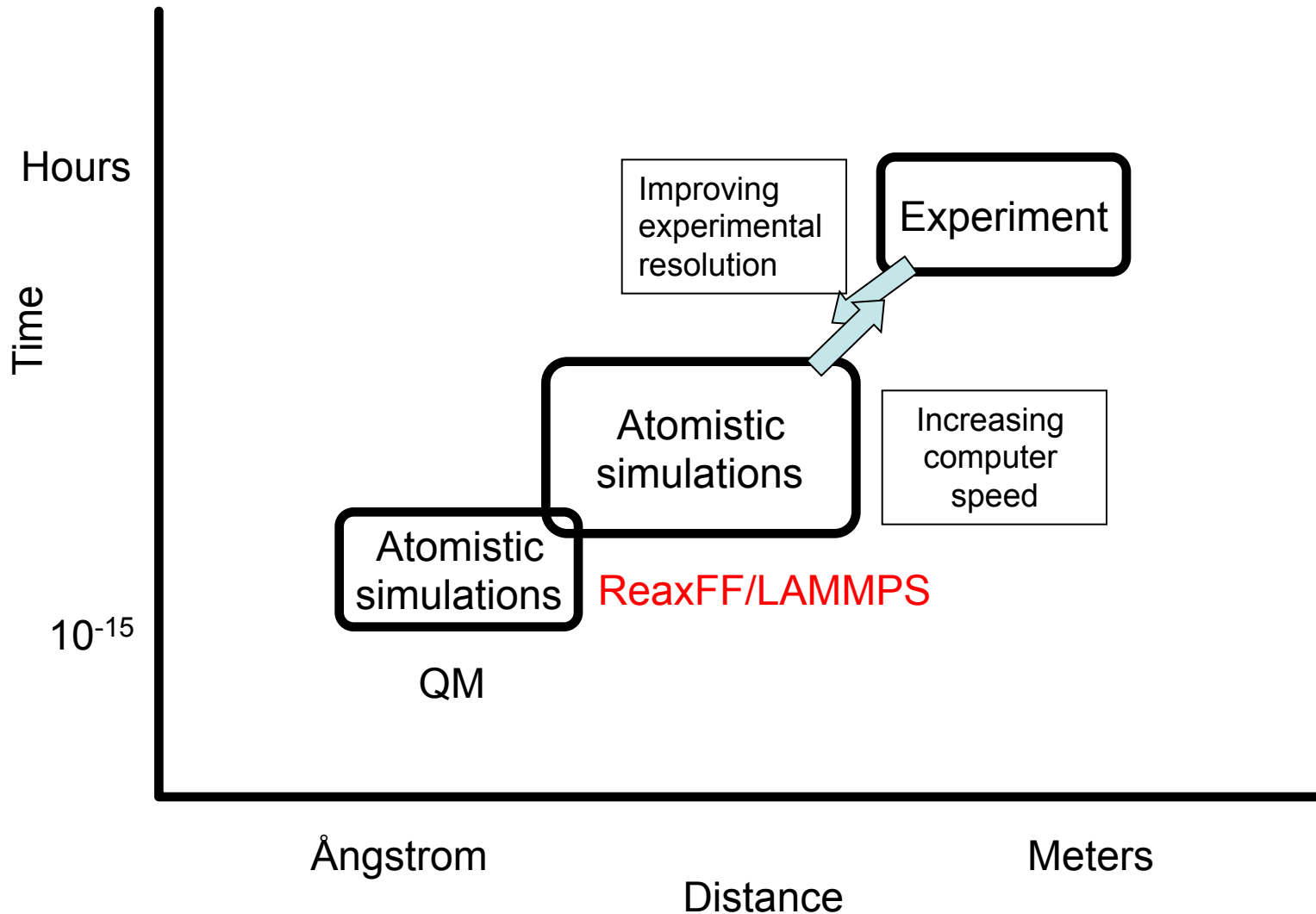


ReaxFF structure of a TiO<sub>2</sub> nanoparticle in water (by Murali Raju; Raju et al. JPC-C 2013)

# Solving the size/time gap between simulation and experiment

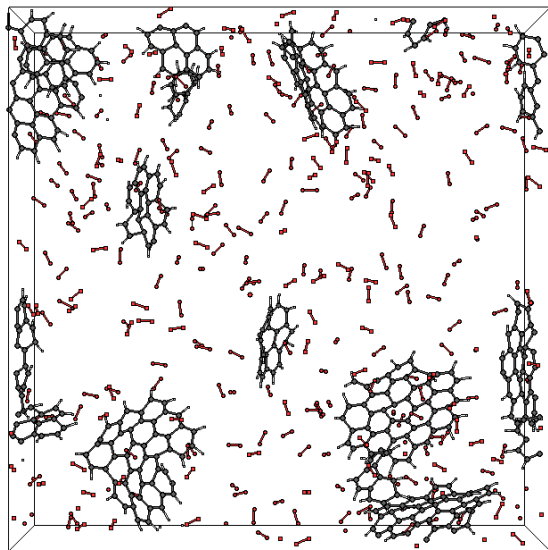


# Solving the size/time gap between simulation and experiment

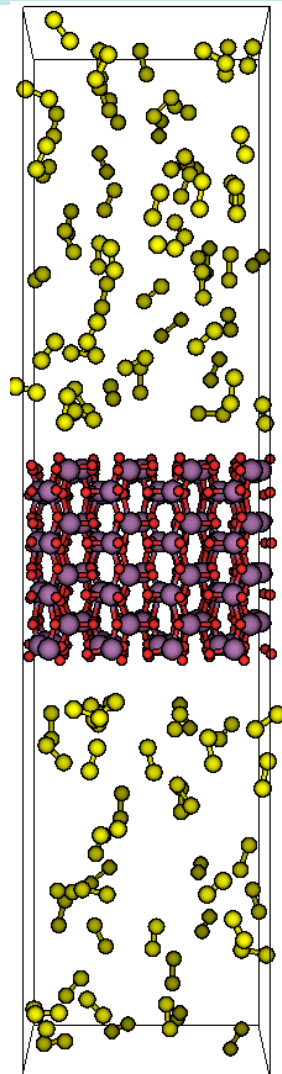


# Outline

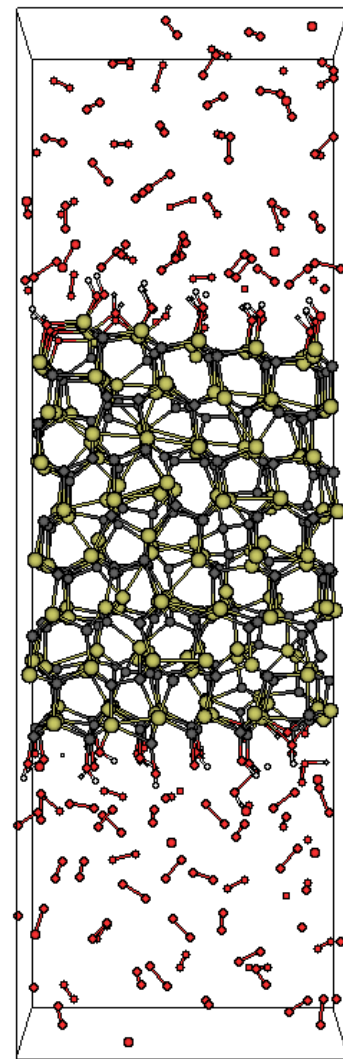
- The ReaxFF reactive force field
- Application to combustion reactions
- Application to aqueous-phase reactions
- New ReaxFF simulation options – soon in LAMMPS (?)
- Summary



ReaxFF MD simulation  
of char combustion at  
 $T=2500\text{K}$



ReaxFF MD simulation  
of  $\text{S}_2$  gas reacting with a  
 $\text{MoO}_3$  slab at  $T=1000\text{K}$

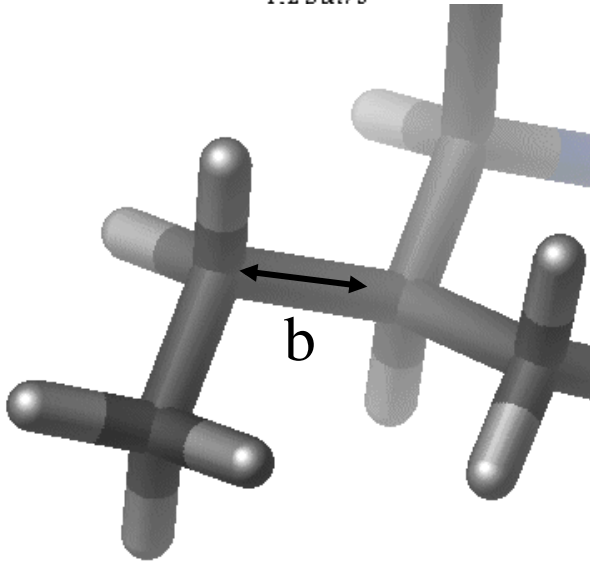


ReaxFF MD simulation  
of the oxidation of a  
 $\text{SiC}$ -slab at  $T=3000\text{K}$

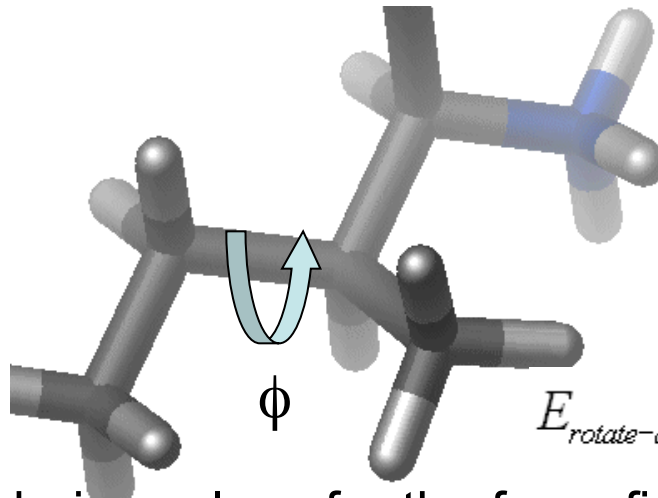
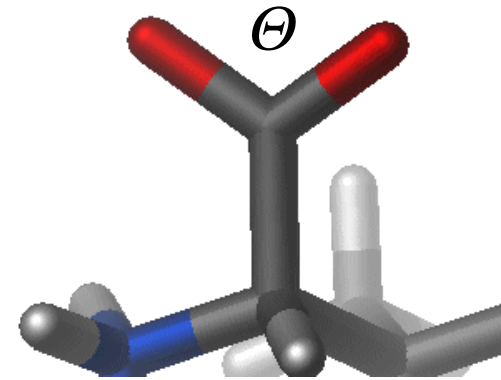


# Force field methods

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



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



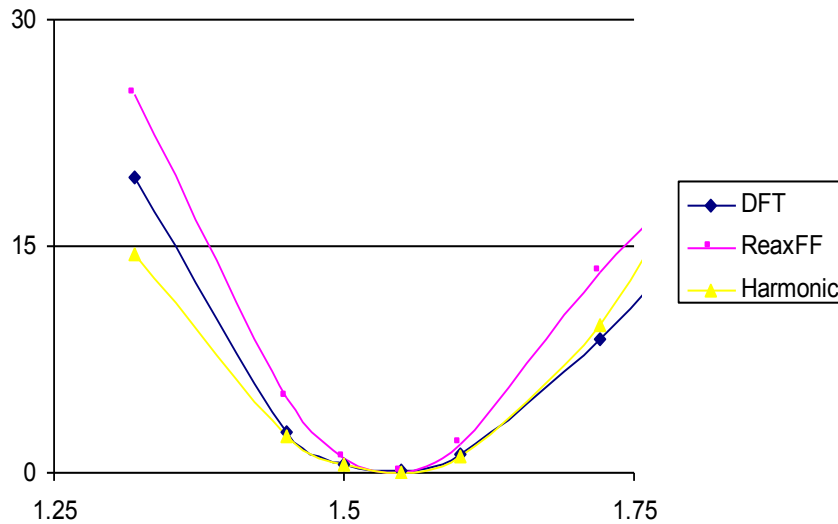
$$E_{\text{rotate-along-bond}} = \sum_{1,4 \text{ pairs}} K_\phi (1 - \cos(n\phi))$$

- 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

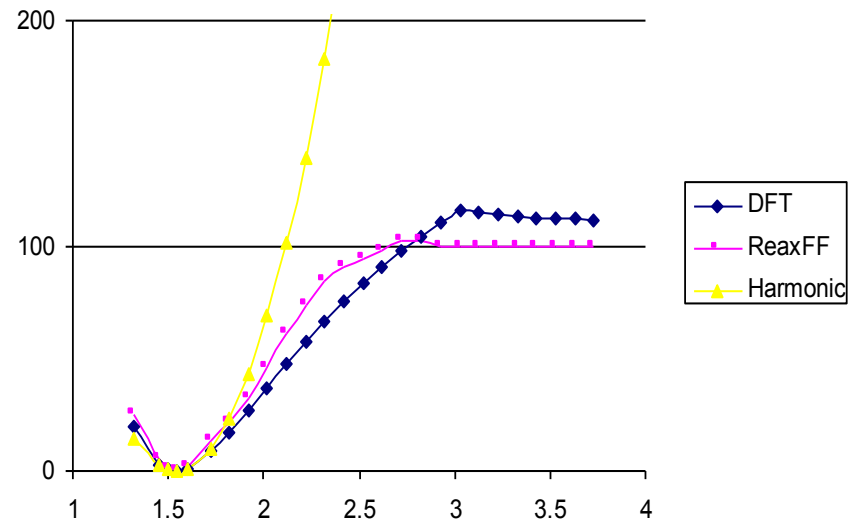
# Failure of the harmonic model

## 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.

# Key features of ReaxFF

- To get a smooth transition from nonbonded to single, double and triple bonded systems ReaxFF employs a bond length/bond order relationship [1-3]. Bond orders are updated every iteration.
- All connectivity-dependent interactions (i.e. valence and torsion angles, H-bond) are made bond-order dependent, ensuring that their energy contributions disappear upon bond dissociation.
- Nonbonded interactions (van der Waals, Coulomb) are calculated between **every** atom pair, irrespective of connectivity. Excessive close-range nonbonded interactions are avoided by shielding.
- ReaxFF uses EEM, a geometry-dependent charge calculation scheme that accounts for polarization effects [4].

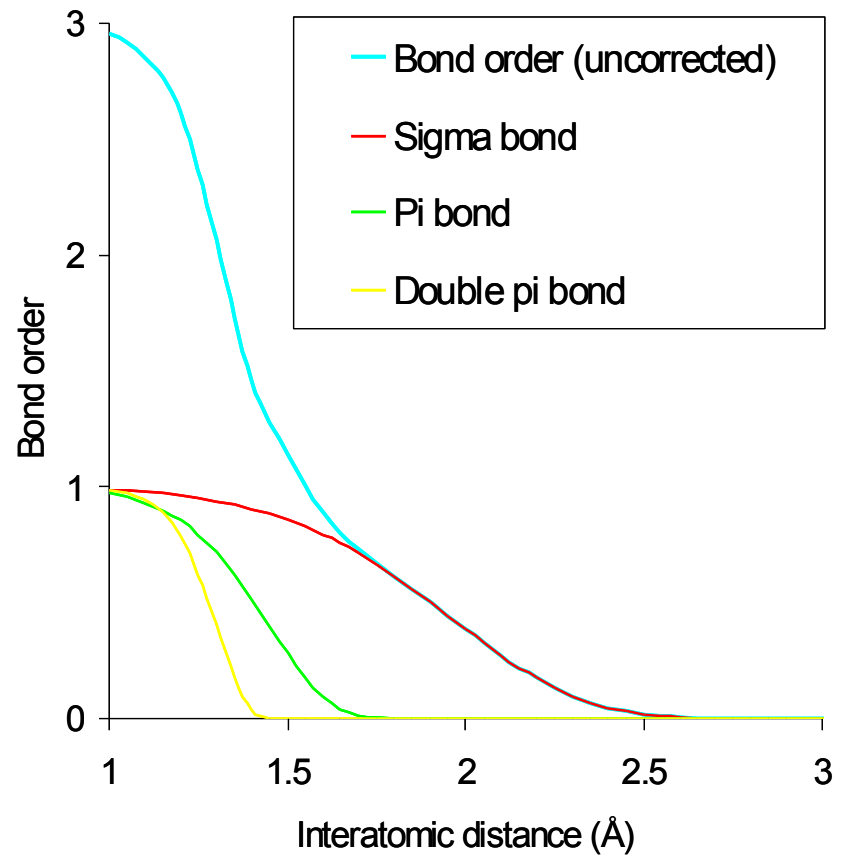
1. Brenner, D. W., (1990) Physical Review B **42**, 9458-9471
2. Tersoff, J., (1988) Physical Review Letters **61**, 2879-2882.
3. Abell, G. C., (1985) Physical Review B 31.
4. Mortier, W. J., Ghosh, S. K., and Shankar, S. (1986) JACS **108**, 4315-4320.

## 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.

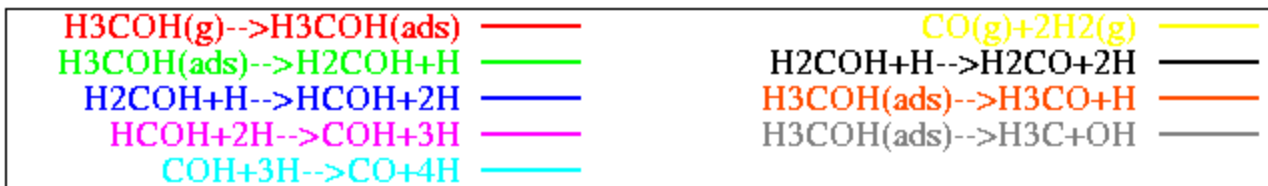
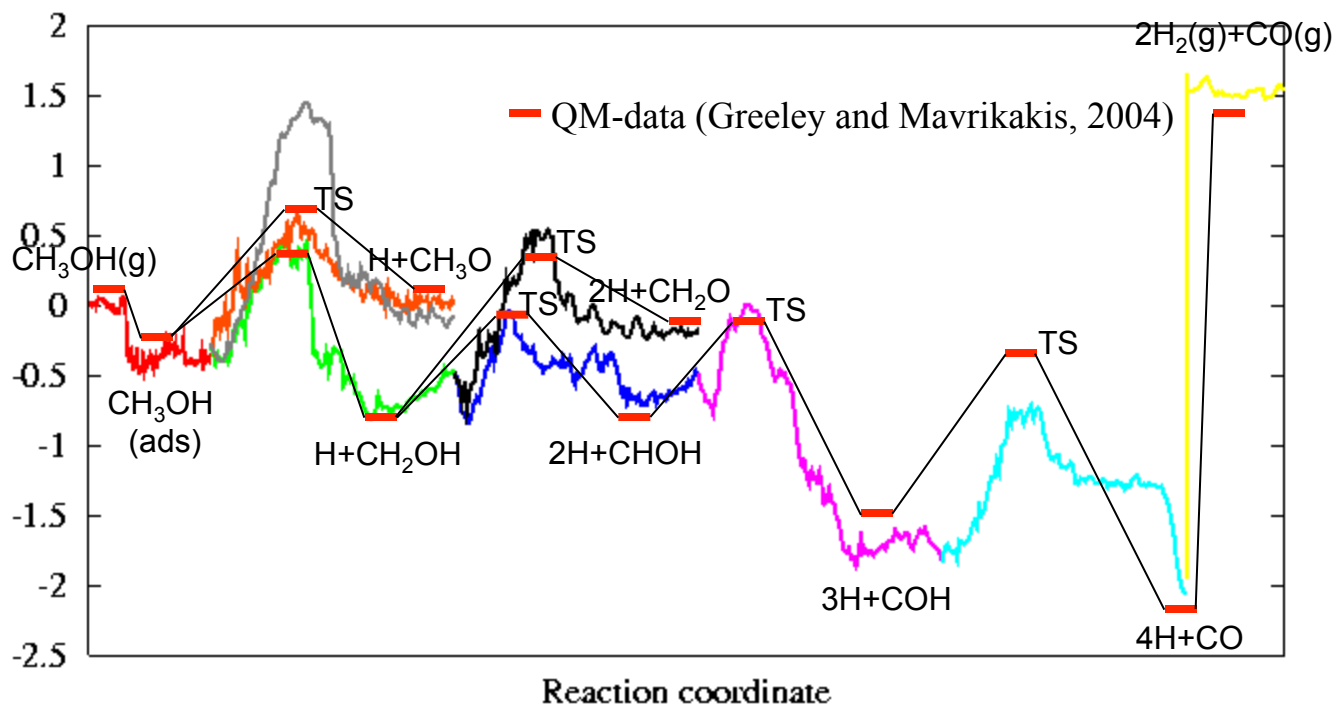
## Calculation of bond orders from interatomic distances

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



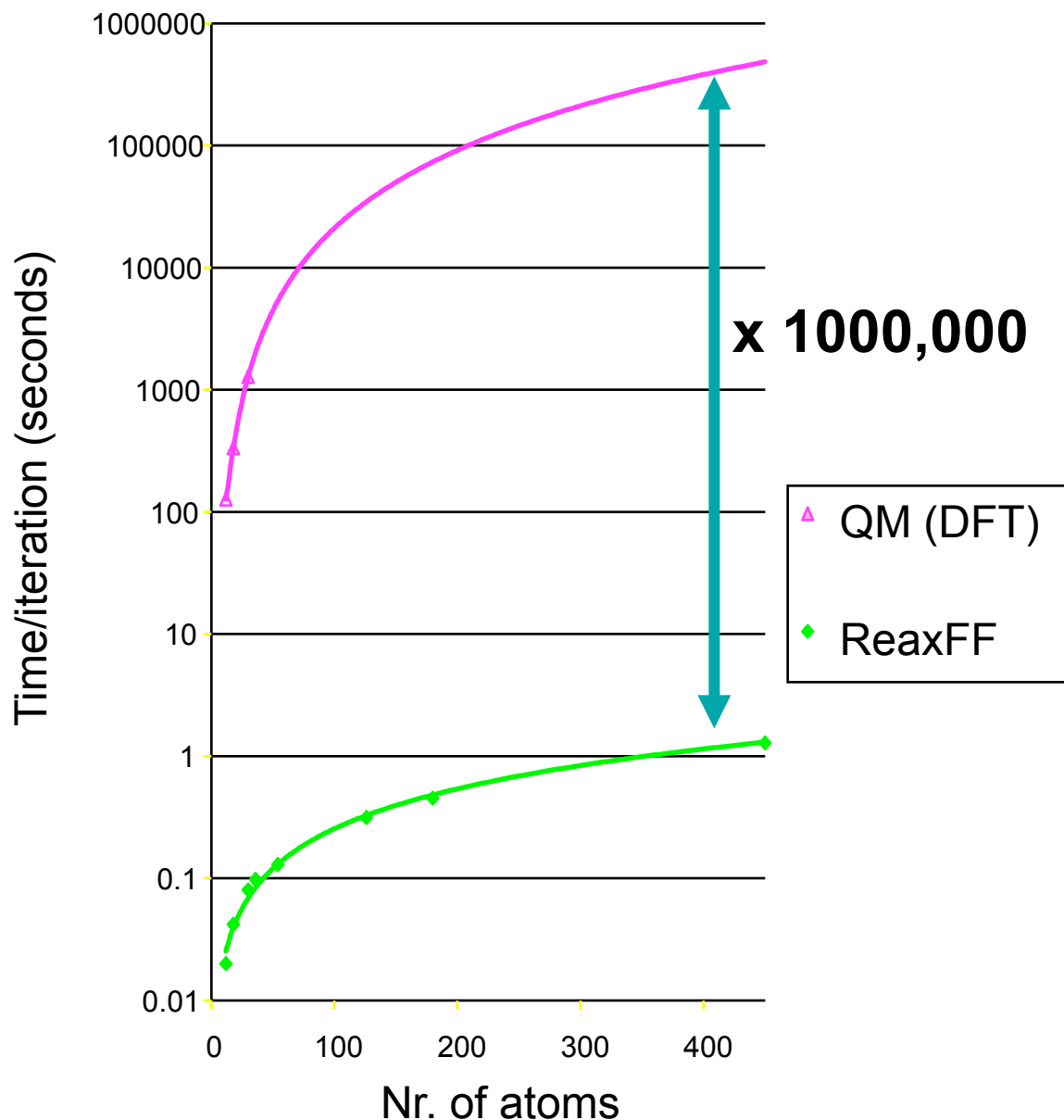
# QM/ReaxFF methanol reaction pathways

Methanol reaction on Pt[111] surface

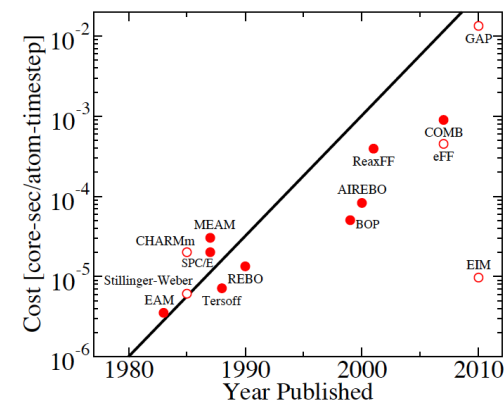


- Good agreement between ReaxFF and QM for entire reaction path

# 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)



Steve Plimpton and Aidan Thompson, MRS review 2012



# 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 250 research groups
- Over 150 publications in peer-reviewed journals
- Parallel ReaxFF (LAMMPS/ReaxFF) available as open-source
- Integrated in ADF/BAND graphical user interface

## ReaxFF transferability

The periodic table is color-coded to show which groups of elements are currently described by ReaxFF. The legend indicates the following categories:

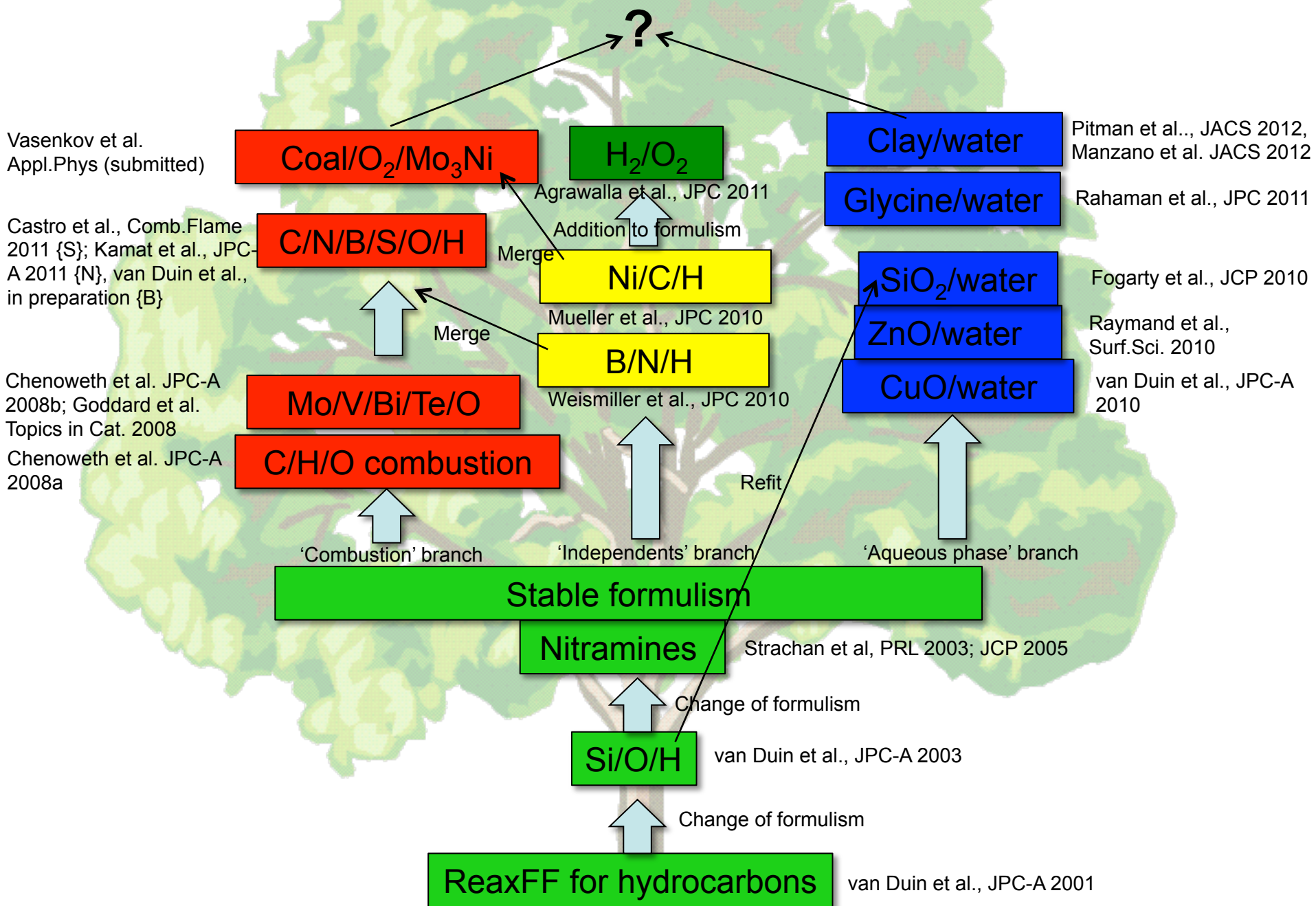
- alkali metals (orange)
- alkaline earth metals (light orange)
- transition metals (purple)
- other metals (light purple)
- other nonmetals (red)
- halogens (green)
- noble gases (blue)
- lanthanides (yellow)
- actinides (light blue)

Elements not currently described by ReaxFF are shown in grey. The table includes element symbols, atomic numbers, and group/period labels.

period	group	1*	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
		1a	2a	3a**	4a	5a	6a	7a	8a	9a	10a	11a	12a	IIIa	IVa	Va	VIa	VIIa	VIIIa
1		H	He																
2		Li	Be											B	C	N	O	F	Ne
3		Na	Mg	Al	Si	P	S	Cl	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

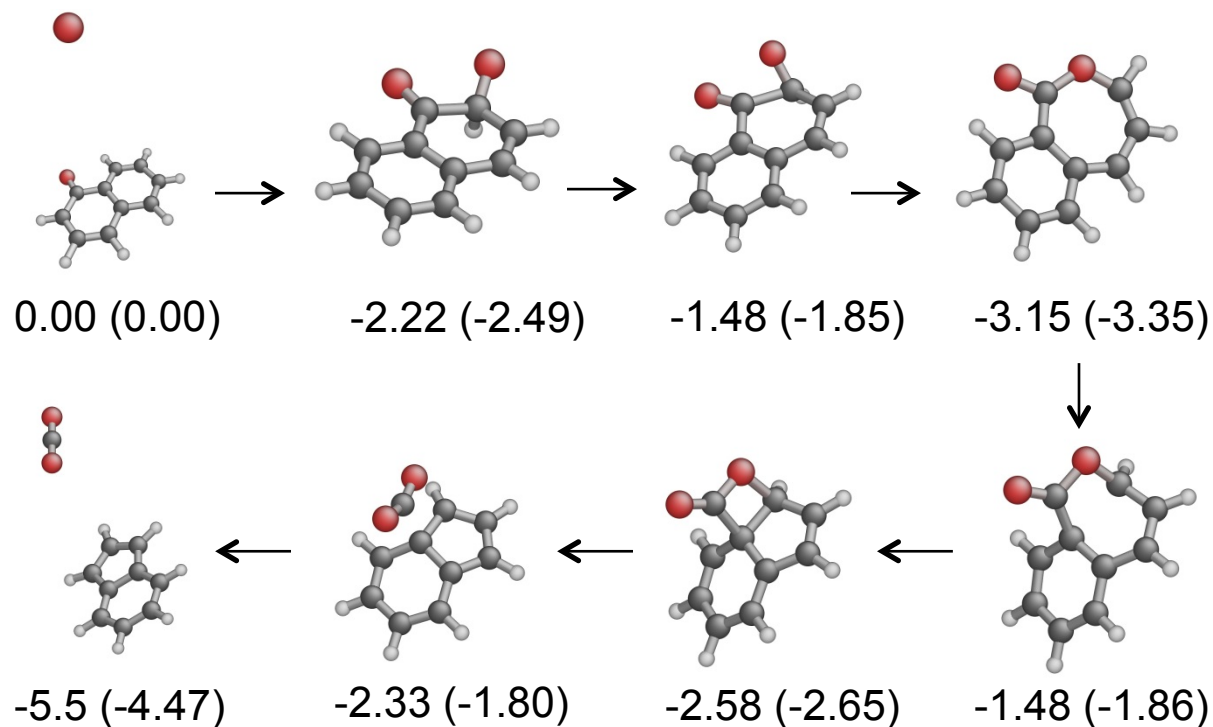
# ReaxFF development tree: towards complex materials



# Graphene oxidation simulations

With Sriram Srinivasan and Tom Schwartzentruber

## 1. Force field development

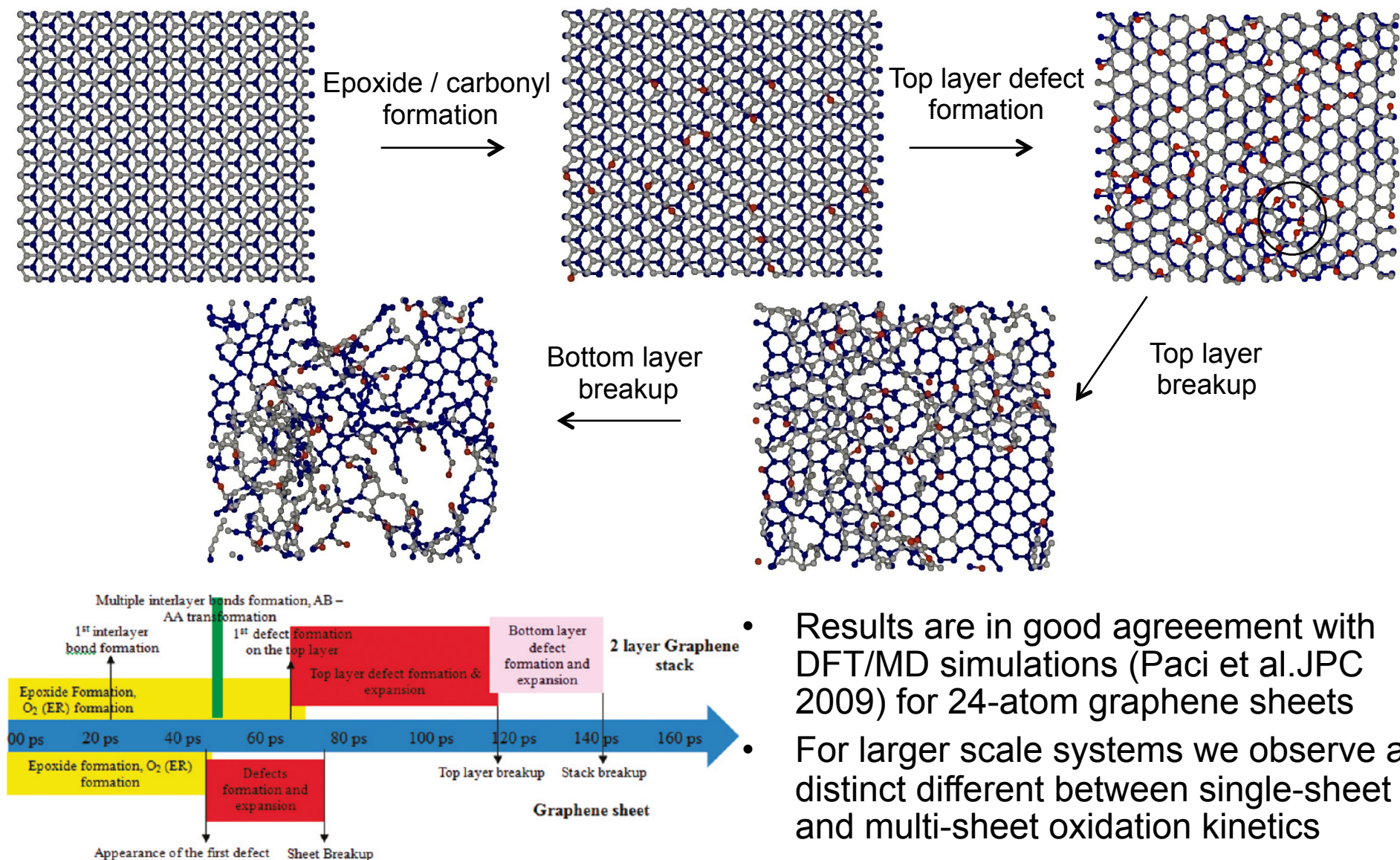


dE in eV/mol;  
DFT [2] results in brackets

[1] Chenoweth K., van Duin A. C. T., Goddard W. A., *J. Phys. Chem. A* **2008**, 112, 1040–1053

[2] Orrego J. F., Zapata, F., Truong T. N., Mondragón F., *J. Phys. Chem. A* **2009**, 113 (29), 8415-8420

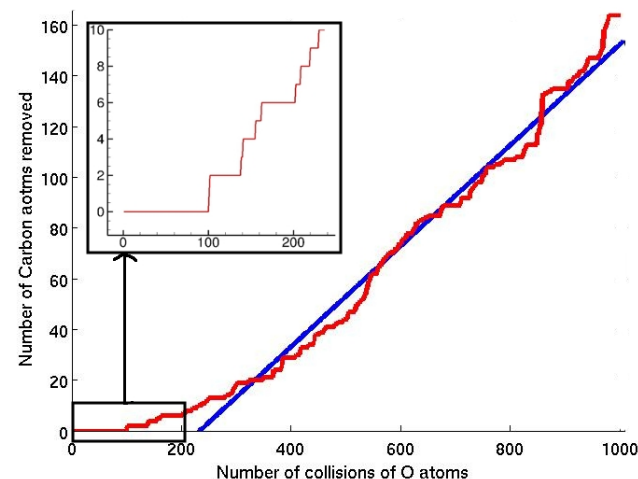
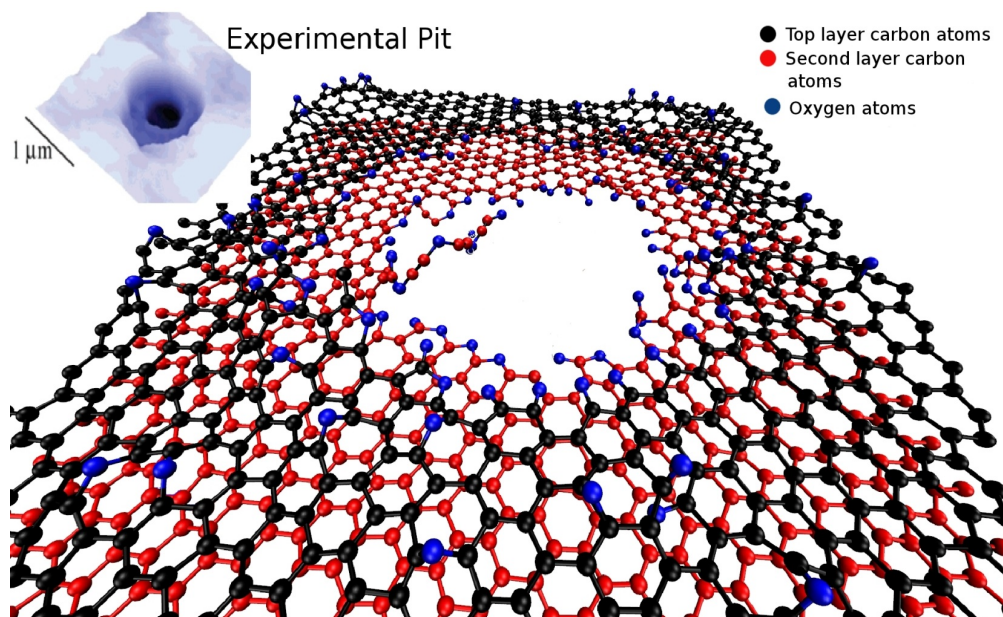
## 2. Validation: Process of graphite erosion



- Results are in good agreement with DFT/MD simulations (Paci et al. JPC 2009) for 24-atom graphene sheets
- For larger scale systems we observe a distinct difference between single-sheet and multi-sheet oxidation kinetics



### 3. Application: Process of HOPG erosion, comparison with experiment and links to coarse-grain simulations

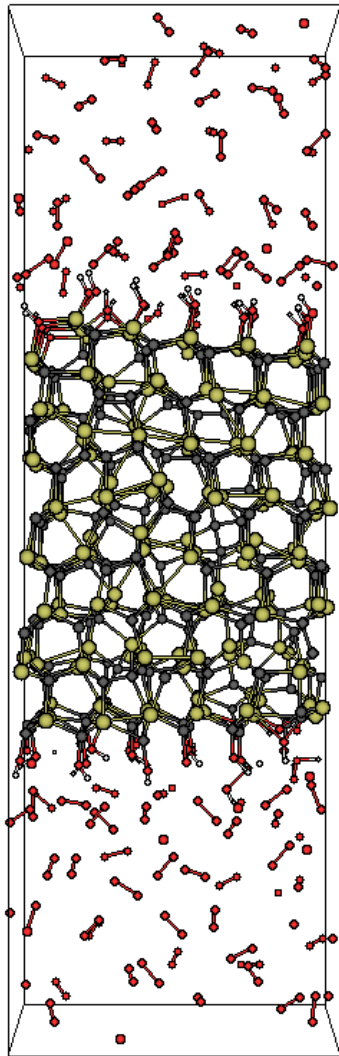


- Molecular beam experiments on HOPG sample showed a pitting behavior. Large shallow pits were observed on the surface of the sample.
- Rate of removal of carbon atoms from the graphite specimen: 1 carbon atom for every 5 oxygen atom collisions

Nicholson K.T., Minton T.K., Seibner S.J., *J. Phys. Chem. B*, **2005**, 109, 8476

Poovathingal S., Schwartzentruber T.E., Goverapet Srinivasan S., van Duin A.C.T., *J. Phys. Chem. C*, **2013**, 117, 2692

# Increasing complexity: Silicon carbide oxidation [1,2]



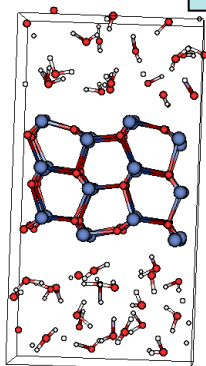
- Oxidation of a SiC-slab results in the formation of a protecting SiO<sub>2</sub> layer and a simultaneous phase separation, results in the formation of an amorphous graphitic phase
- Gas phase contains early carbon oxidation products (CO, CO<sub>2</sub>), but graphitic phase remains unoxidized for the duration of the MD-simulations

[1] Newsome, D., Sengupta, D., and van Duin, A.C.T., **2013**. Journal of Physical Chemistry C accepted for publication.

[2] Newsome, D., Sengupta, D., Foroutan, H., Russo, M. F., and van Duin, A. C.T. Journal of Physical Chemistry **2012**, *116*, 16111-16121.

ReaxFF MD simulation  
of the oxidation of a  
SiC-slab at T=3000K

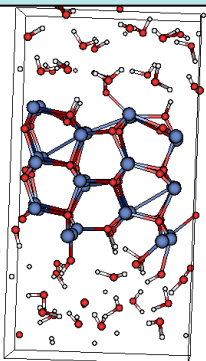
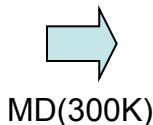
# Aqueous phase reactions and surface chemistry



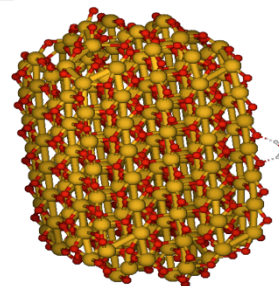
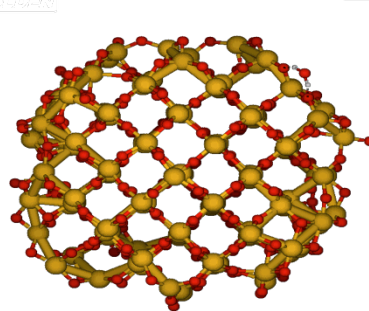
ZnO/H<sub>2</sub>O

**Cu/Zn oxides**

With Raymand & Hermannsson (Uppsala)



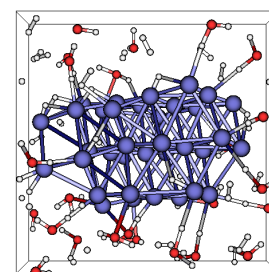
Partially hydroxyl  
covered surface



With Sung-Yup Kim & Jim Kubicki (PSU)

**Water/TiO<sub>2</sub> interactions**

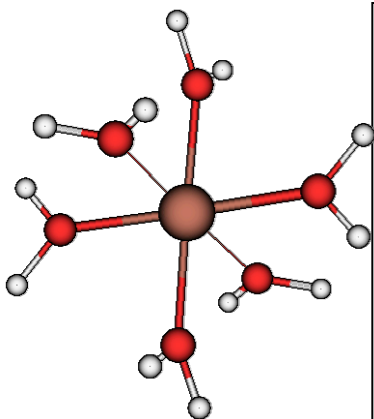
**ReaxFF for water**



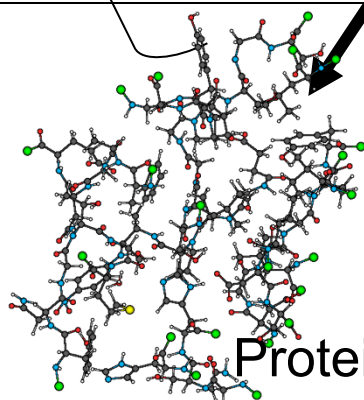
**Pt/Ni fuel cells**

**Nafion fuel cell**

**Dendrimers/metal  
cations**



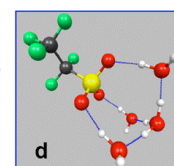
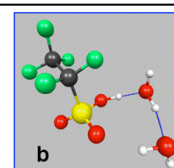
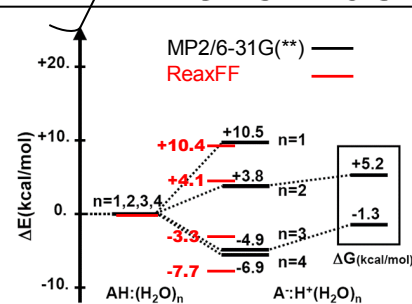
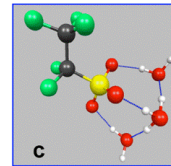
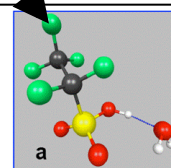
Jahn-Teller distorted  
Cu(H<sub>2</sub>O)<sub>6</sub><sup>2+</sup>-cluster



**Proteins**

With Ramie & Doren(Delaware)

**Enzymes/  
DNA/  
organic  
catalysis**

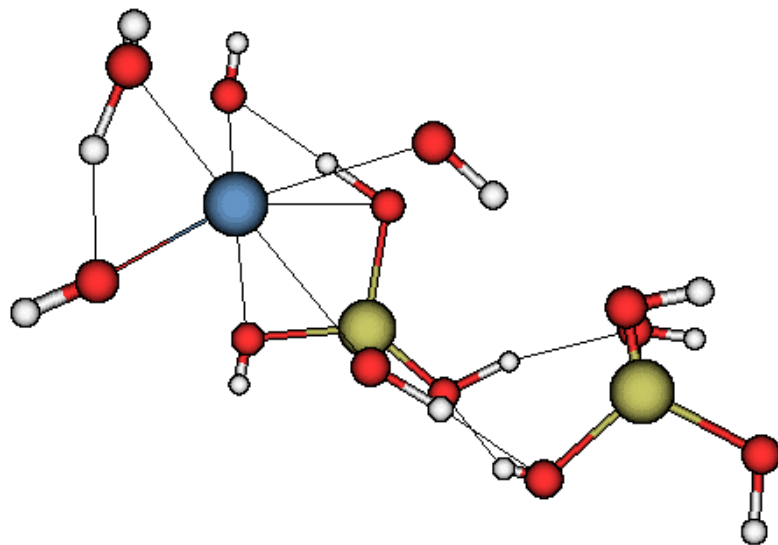


**Phosphates/sulfonates**

With Ram Devanathan (PNNL)

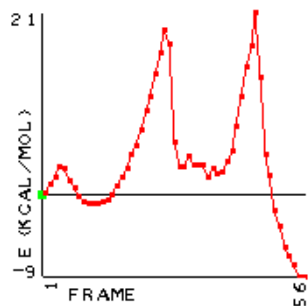


# Applications to water/silica chemistry



$\text{Si(OH)}_4$  dimerization catalyzed by a  $\text{Ca(OH)}_2 \cdot 2\text{H}_2\text{O}$  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  $T=25\text{K}$  with sliding restraint to drive reaction  
5000 iterations  
CPU-time (this laptop) 35 seconds

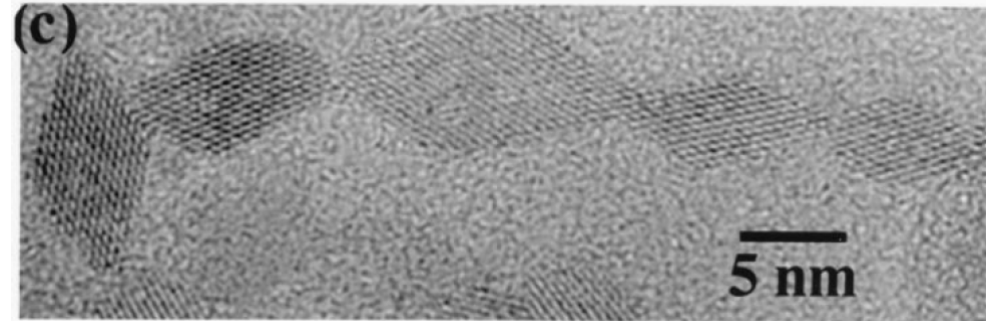
[1] Criscenti and Kubicki, J.Phys.Chem.A 2006

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

# Oriented attachment in Titania Nanoparticles

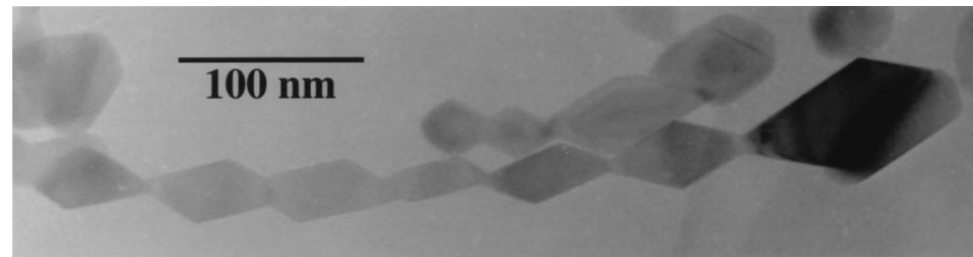
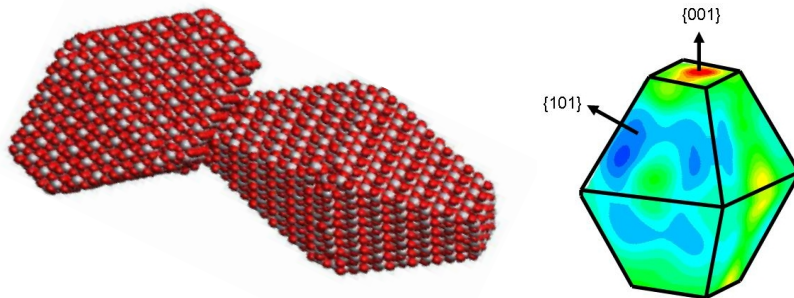
With Murali Raju and Kristen Fichthorn

- Oriented attachment occurs most commonly on  $\{112\}$ , occasionally on  $\{001\}$ , and rarely on  $\{101\}$ .
- This mechanism effectively serves to reduce overall surface energy by eliminating the surfaces at which the crystallites join



five primary crystallites forming a single crystal via oriented attachment

Preferential Alignment in vacuum



TEM micrograph of a single crystal of anatase that was hydrothermally coarsened in 0.001 M HCl.

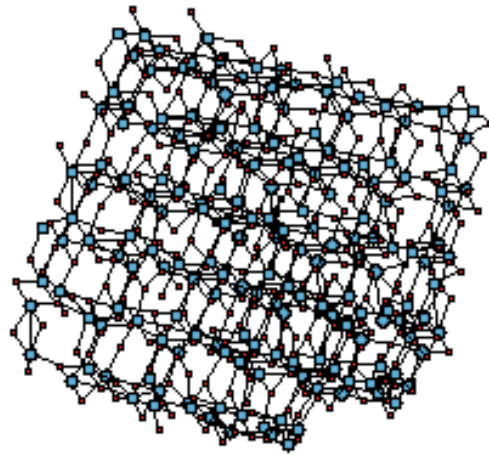
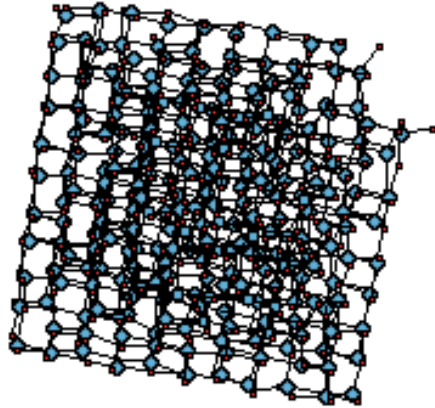
M. Alimohammadi and K. Fichthorn, *Nano Lett.* 9, 4198 (2009).

R. Penn and J. Banfield, *Geochim. Cosmochim. Acta* 63, 1549 (1999).

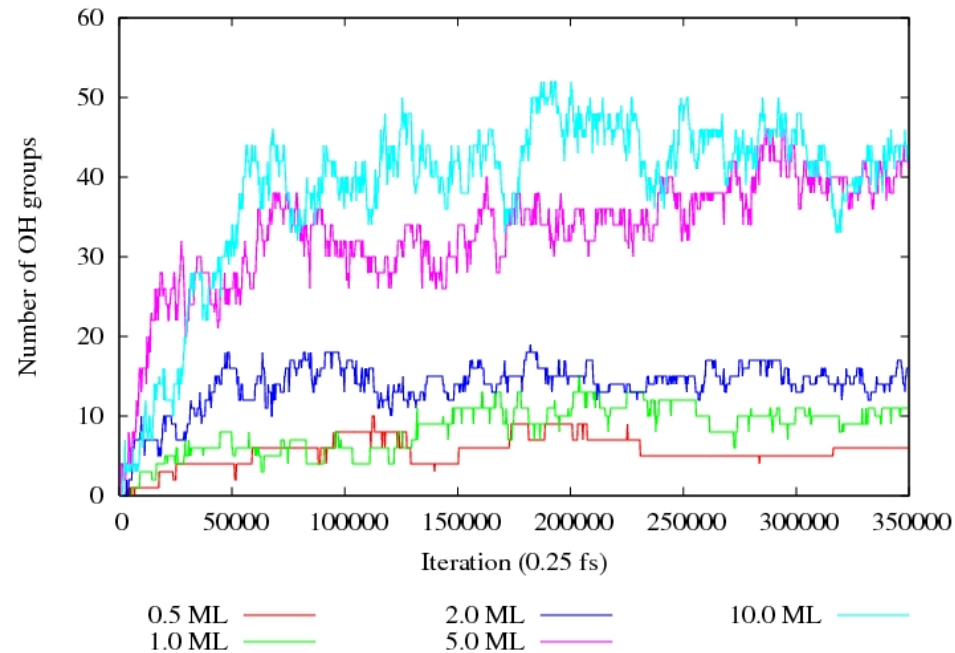
A Review on Oriented Attachment:

M. Niederberger and H. Cölfen, *Phys. Chem. Chem. Phys.* 8, 3271 (2006).

# Behavior in Vacuum: No Oriented Attachment



# Water Dissociation on Anatase Nanoparticles



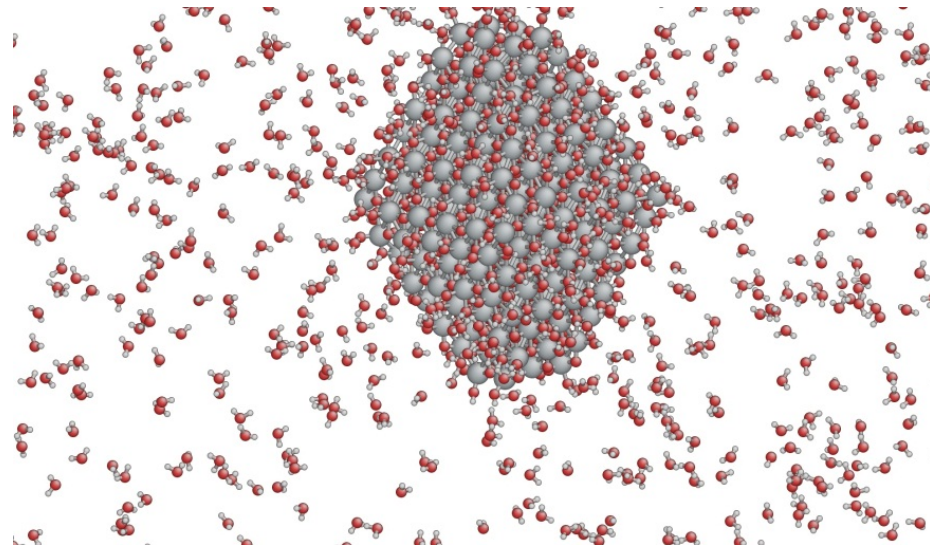
## Hypothesis

Solvent mediates growth by oriented attachment through adsorbed surface groups; OH groups and adsorbed  $\text{H}_2\text{O}$ .

Investigate amount of solvent needed to saturate the nanoparticle surface with surface groups.

## Hydroxyl coverage on an anatase nanoparticle at 1100K

- The nanoparticle surface is saturated with OH groups around a coverage of 5 ML.
- Run simulations with a coverage of 5 ML to aid in faster diffusion of nanoparticles.



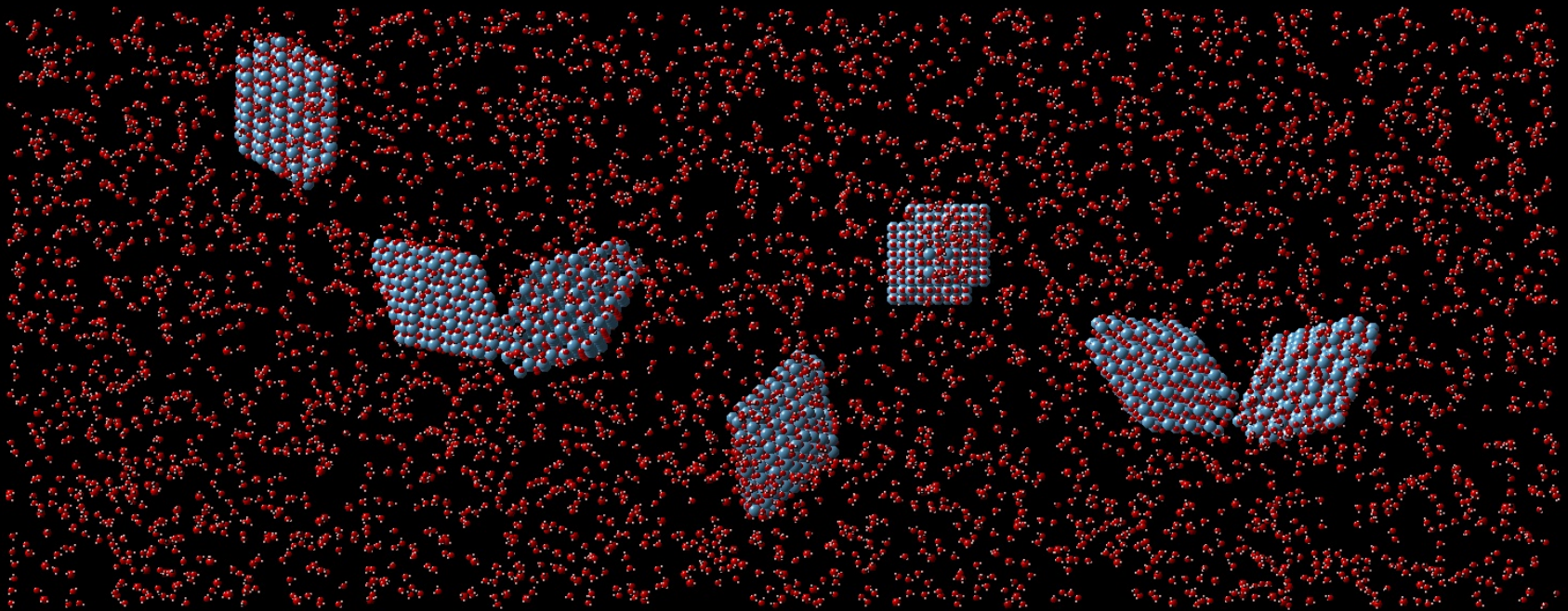


# Behavior in Water

Simulation Cell: 125 Å x 325 Å x 125 Å

NVT at 1100 K (aid in faster diffusion of nanoparticles)

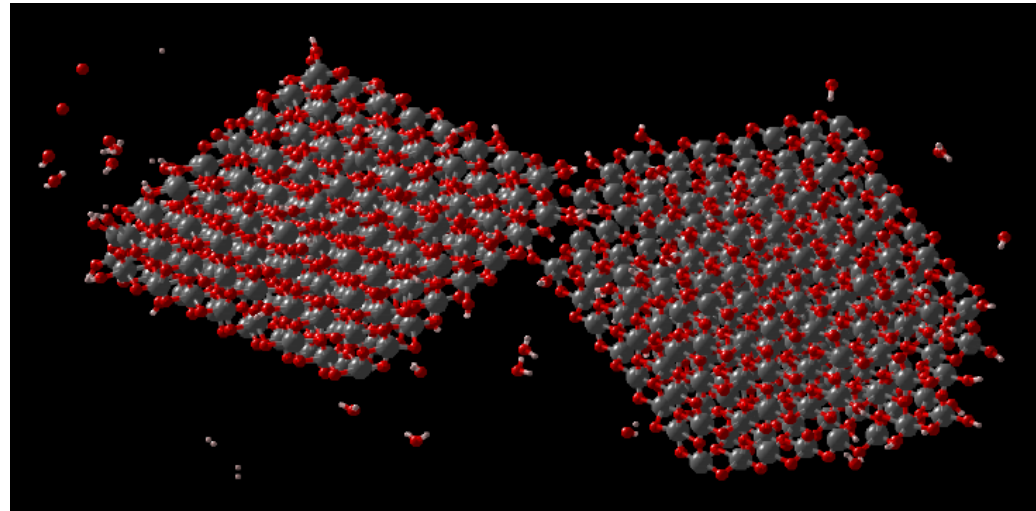
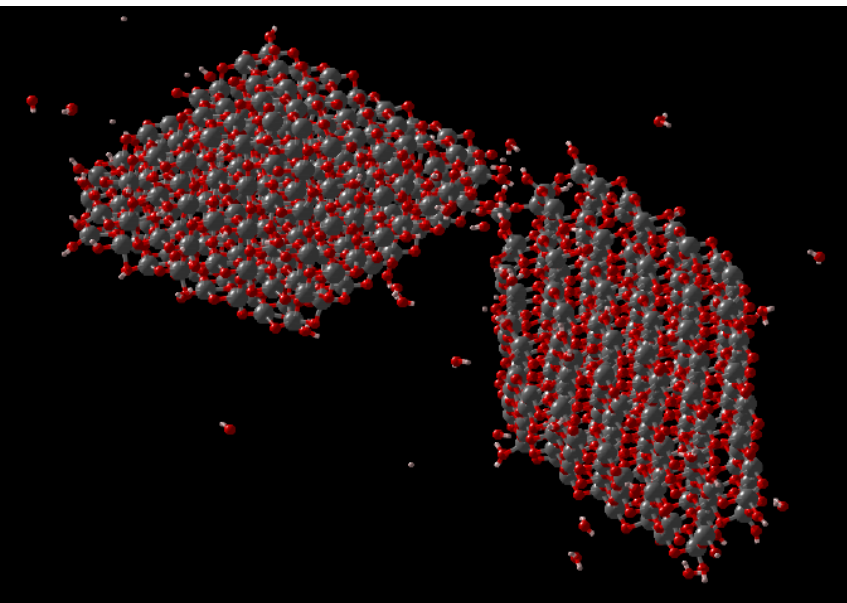
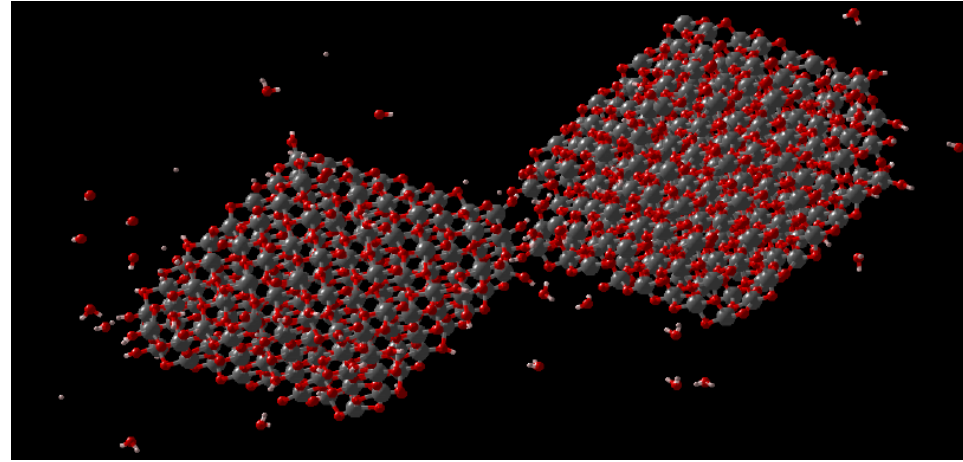
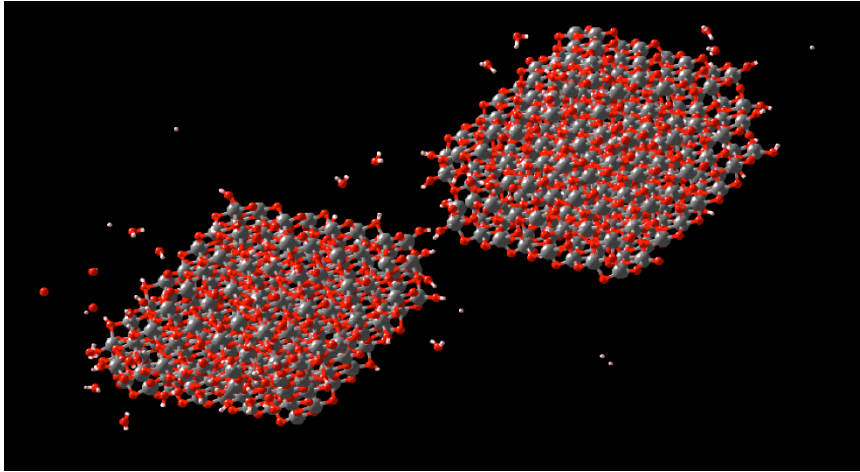
8 - (112) truncated nanoparticles and 4270 - water molecules



# Behavior in Water

## Role of Water -1

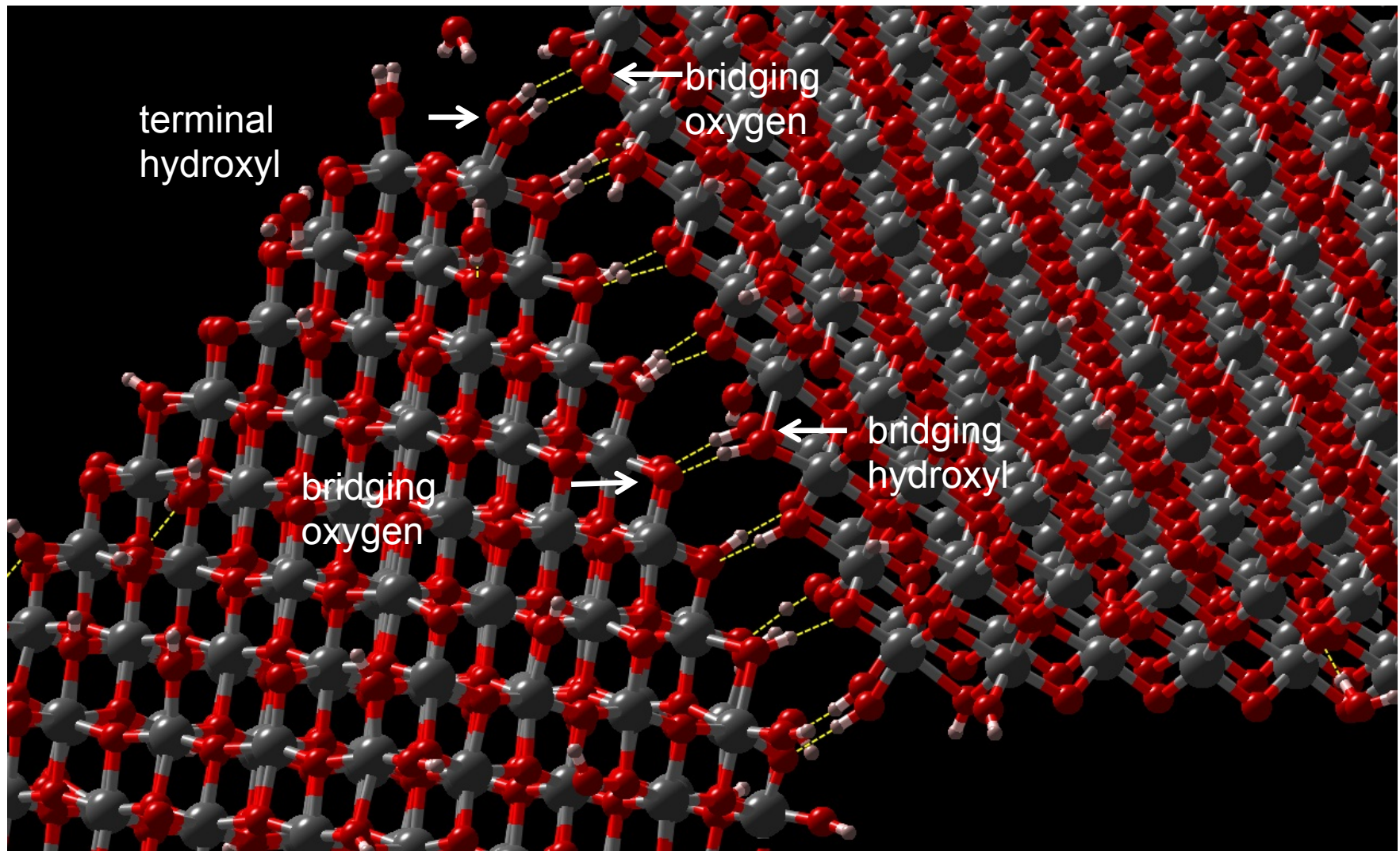
Adsorbed  $\text{H}_2\text{O}$  and OH prevent immediate aggregation





# Nanoparticles Aligned Along (112)

Hydrogen bond

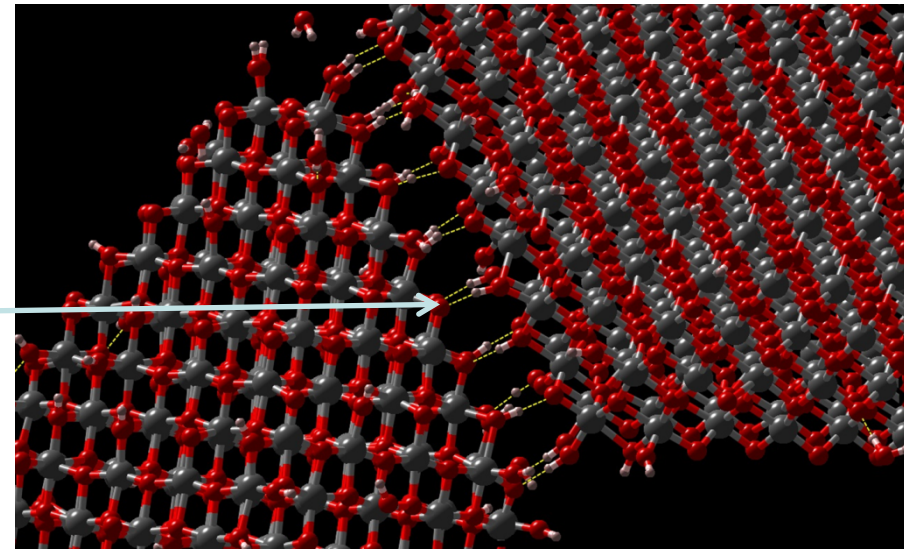
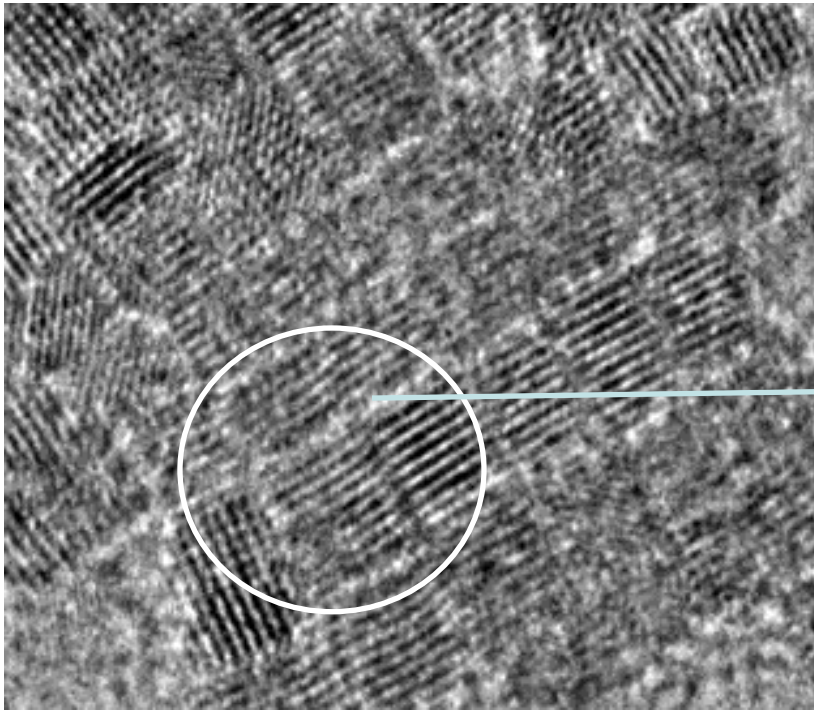


- The nanoparticles slide along each other, making and breaking hydrogen bonds until they align
- Aligning favors the formation of a network of hydrogen bonds between the terminal or bridging hydroxyls on one nanoparticle and the surface oxygens on the other nanoparticle.



# Comparison with Experiment

How does it compare with experiment?



TEM image of 'wet' SnO<sub>2</sub>  
nanoparticles

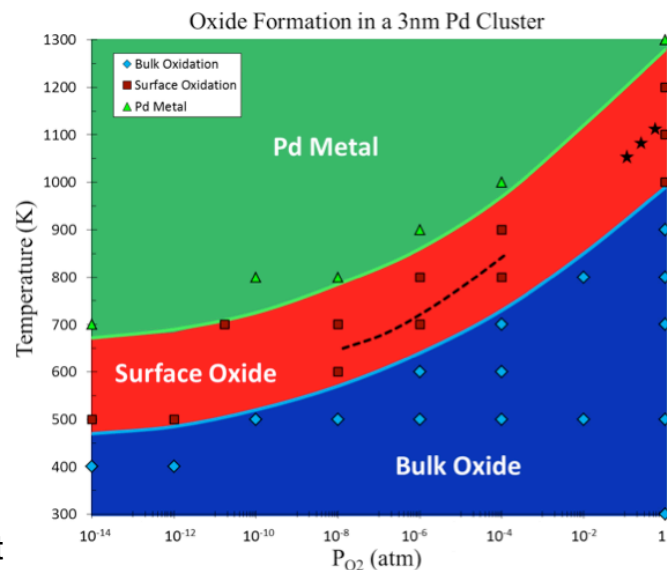
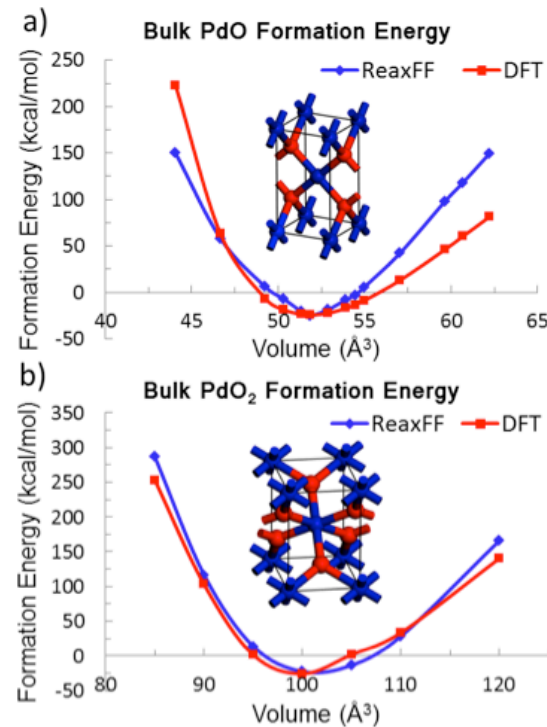
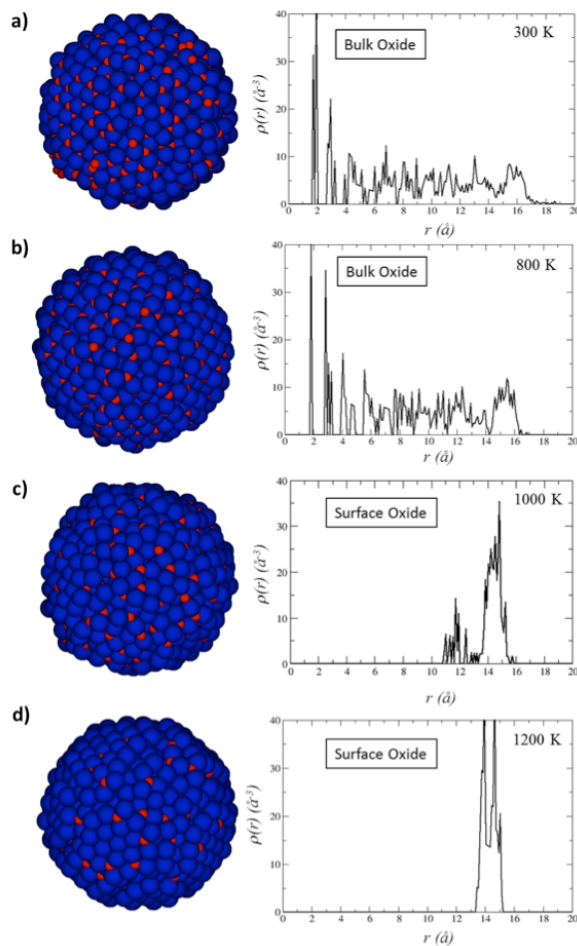
Image Courtesy: Wei Wang, Hsiu-Wen Wang at ORNL

# New ReaxFF simulation options – soon in LAMMPS (?)

## 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  $\text{PdO}_x$  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**, in print

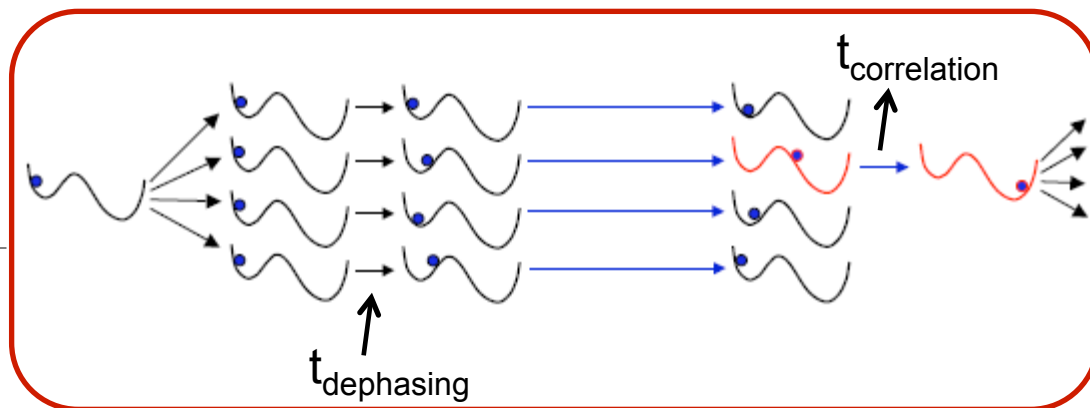
[2] Ketteler, G.; Ogletree, D. F.; Bluhm, H.; Liu, H. J.; Hebenstreit, E. L. D.; Salmeron, M. *J. Am. Chem. Soc.* **2005**, *127*, 18269.

[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

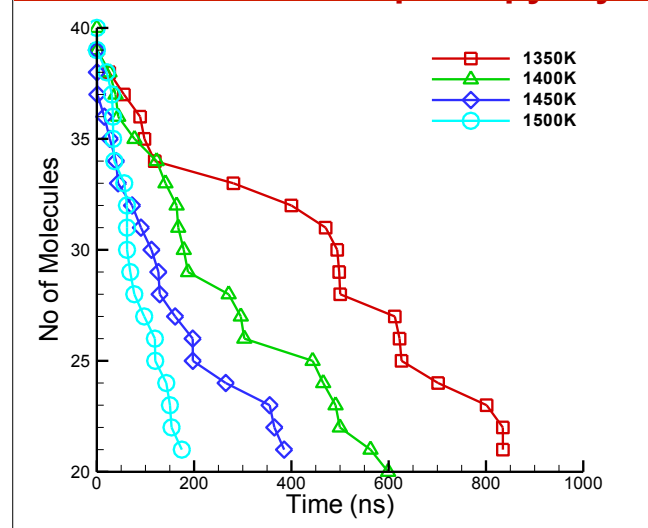
- Infrequent events
- Transitions can be detected
- Exponential distribution of first-escape times
- Correlation time known



- PRD is coupled with REAXFF in LAMMPS 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

# EEM upgrade: 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

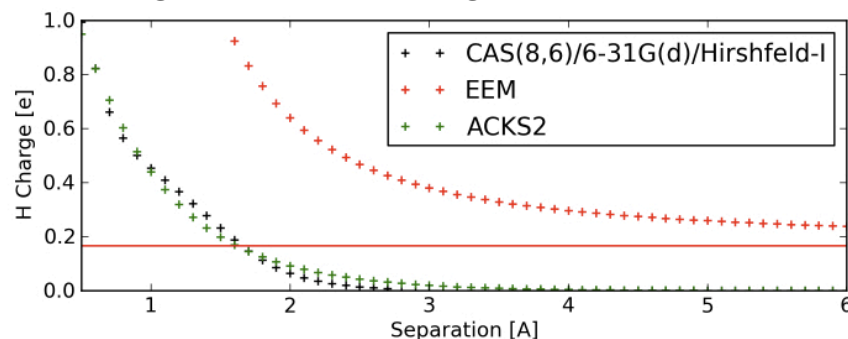
$$- \begin{bmatrix} \eta & -d \\ -d^T & 0 \end{bmatrix} \begin{bmatrix} q \\ \chi_{\text{mol}} \end{bmatrix} = \begin{bmatrix} \chi \\ q_{\text{tot}} \end{bmatrix}$$

## 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>29</sup>


# 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 ? Not very impressive speed-up.
- Ananth Grama-group has recently finished an initial ReaxFF/GPU version, based on C++/ReaxFF version integrated in LAMMPS. Double precision, gcc 4.5.4, CUDA 5.0.
- Purdue/GPU/ReaxFF looks very promising – 4 times faster than best current ReaxFF method for 2000 atoms; looks even better for larger systems (5000-10,000 atoms).
- Needs further development (memory management, parallel GPU)

# 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/LAMMPS allows reactive simulations on  $>> 1,000,000$  atoms, enabling close interaction with experiment

group	1*	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
period	1a	2a	3a	4a	5a	6a	7a	8a	9a	10a	11a	12a	13a	14a	15a	16a	17a	18a
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:

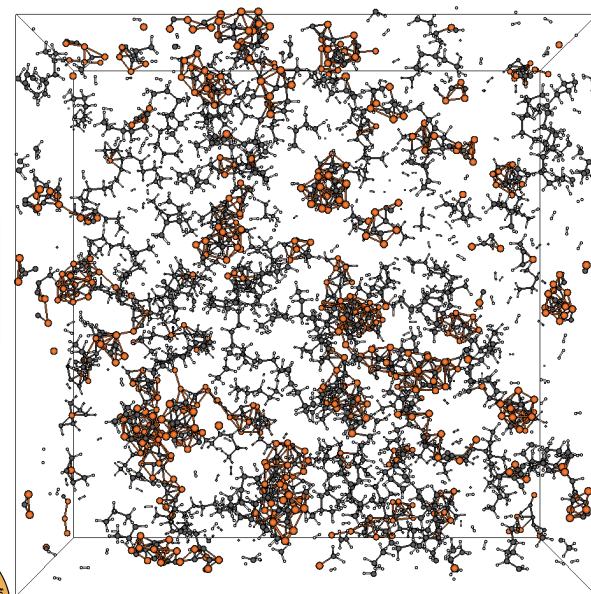
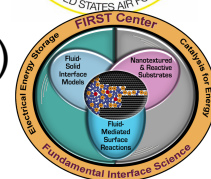
- Jonathan Mathews, Jim Kubicki, Deborah Levin, Rich Yetter and Mike Janik (Penn State)
- Kimberley Chenoweth, Vyacheslav Bryantsev and Bill Goddard (Caltech)
- Aidan Thompson, Steve Plimpton (Sandia), Ananth Grama (Purdue), Metin Aktulga (Purdue) (parallel MD)

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- PSU/KISK startup grant #C000032472



- Illinois Coal grant ICCI 10/7B-3
- NSF (TiO<sub>2</sub>/water, PdO/Ceria)
- NETL/RUA (Fuel catalysis)
- DoE/NETL (Refractory materials)
- AFRL/SBIR (Hydrocarbon cracking)
- 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)

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