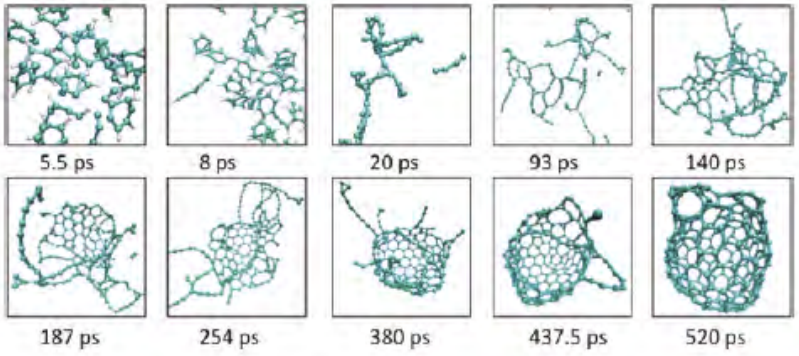

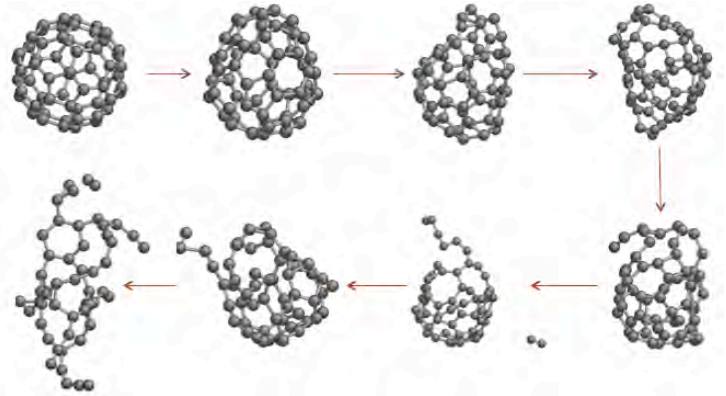

Development, validation and application of ReaxFF reactive force fields for high-temperature surface oxidation

Sriram Srinivasan and Adri van Duin

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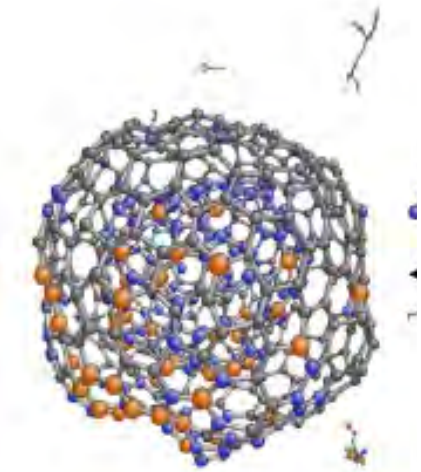
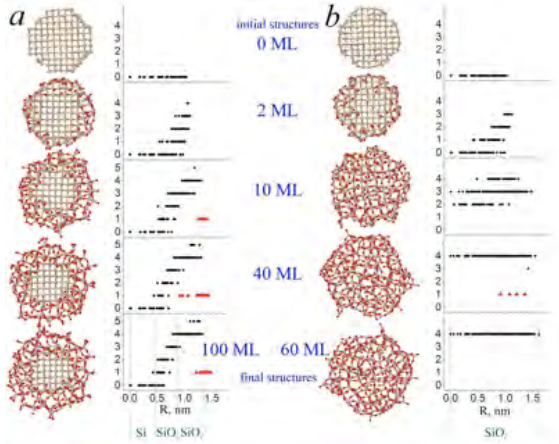
Department of Mechanical and Nuclear Engineering

Penn State

AFOSR/MURI annual review, July 2013

AFOSR Grant# FA9550-10-1-0563





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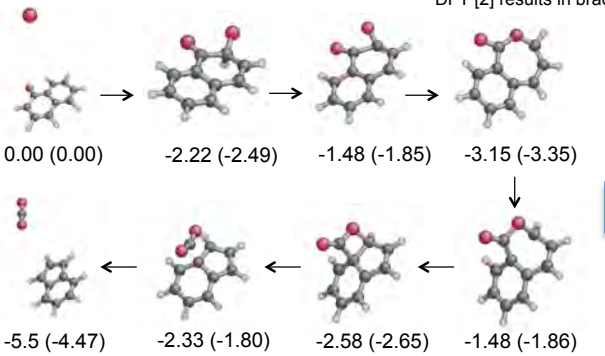
Force field parameterization – comparison with DFT

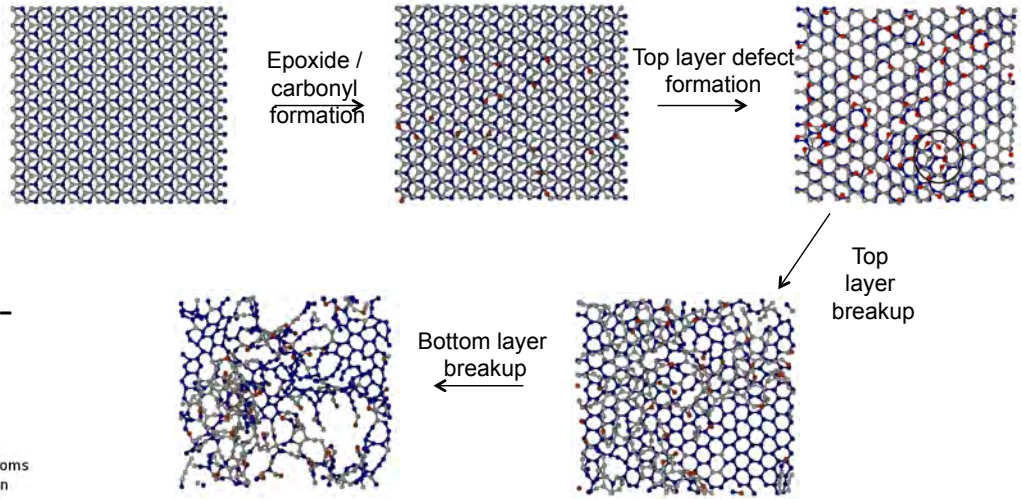
dE in eV/mol;
DFT [2] results in brackets



Kulkarni, A. D., Truhlar, D. G., Srinivasan, S. G., van Duin, A. C. T., Norman, P., and Schwartzentruber, T. E., **2013**. Journal of Physical Chemistry 117, 258-269.

Validation with small-scale Molecular Dynamics

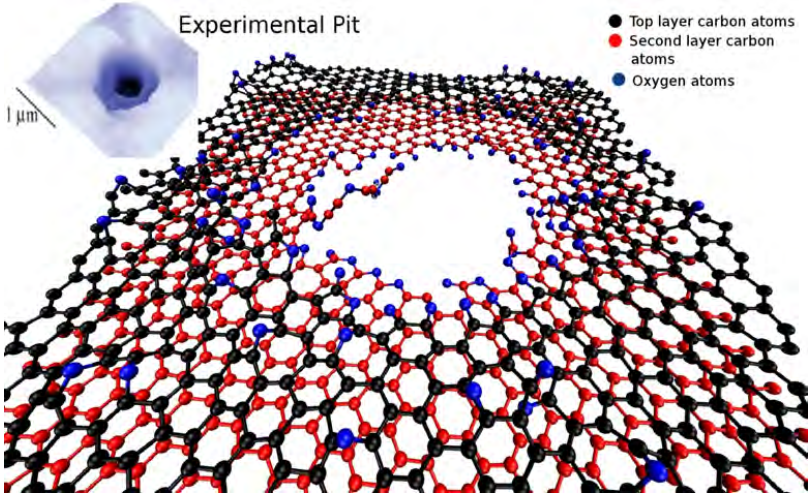
High-temperature oxidation of graphite



Goverapet Srinivasan S., van Duin A. C. T., *J. Phys. Chem. A.*, **2011**, 115, 13269 – 13280

Large-scale parallel molecular dynamics-comparison with experiment

Oxidation pitting of graphite

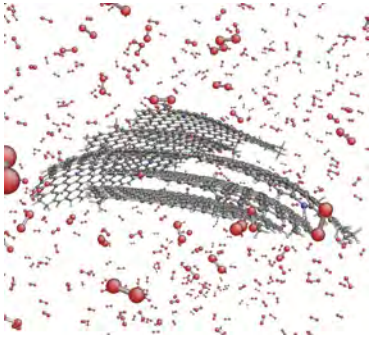
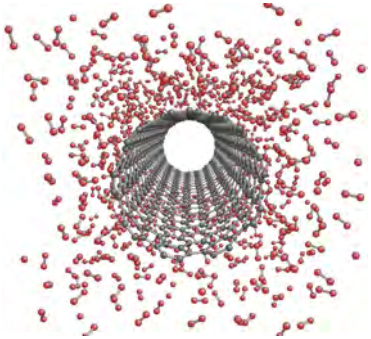
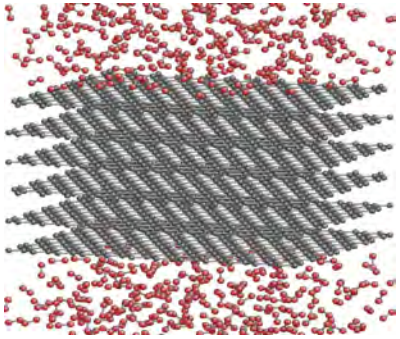
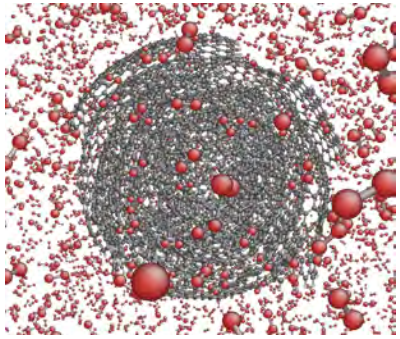


Nicholson K.T., Minton T.K., Seibner S.J., *J. Phys. Chem. B,* **2005,** 109, 8476
Poovathingal S., Schwartzentruber T.E., Goverapet Srinivasan S., van Duin A.C.T., *J. Phys. Chem. C.* **2013**, *117,* 2692

- ReaxFF enables large-scale (>>1000 atoms), long-time (>> 1 ns) simulations of surface chemistry with accuracies approaching DFT-methods, providing a bridge between theory and experiment

Contents

- Introduction to the ReaxFF method
- Graphene oxidation simulations
- Simulating mass-loss kinetics in graphitic materials
- Oxidation kinetics in silica-based materials
- Overview of published and ongoing work related to this project

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UNITED STATES AIR FORCE

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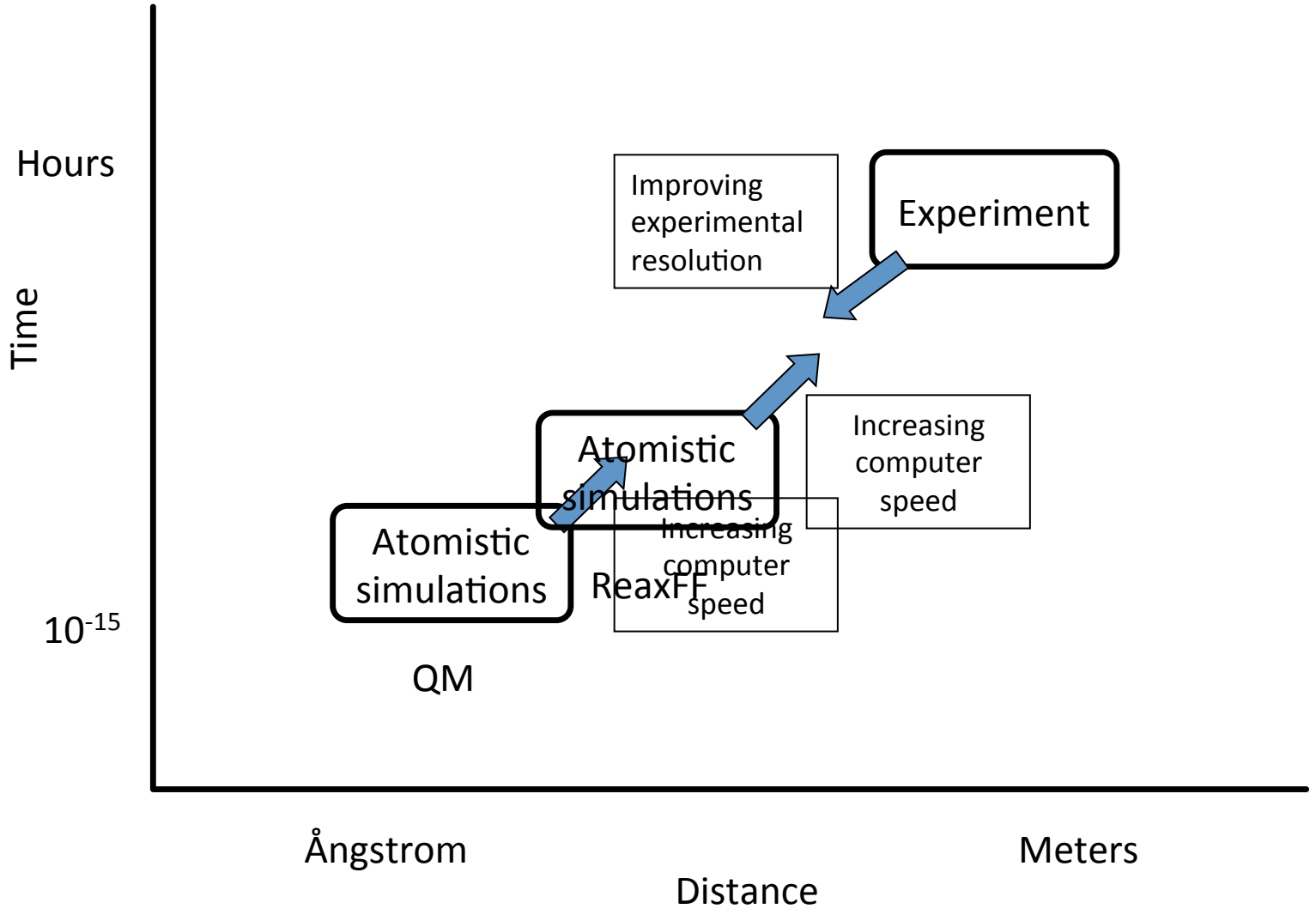
Solving the size/time gap between simulation and experiment



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

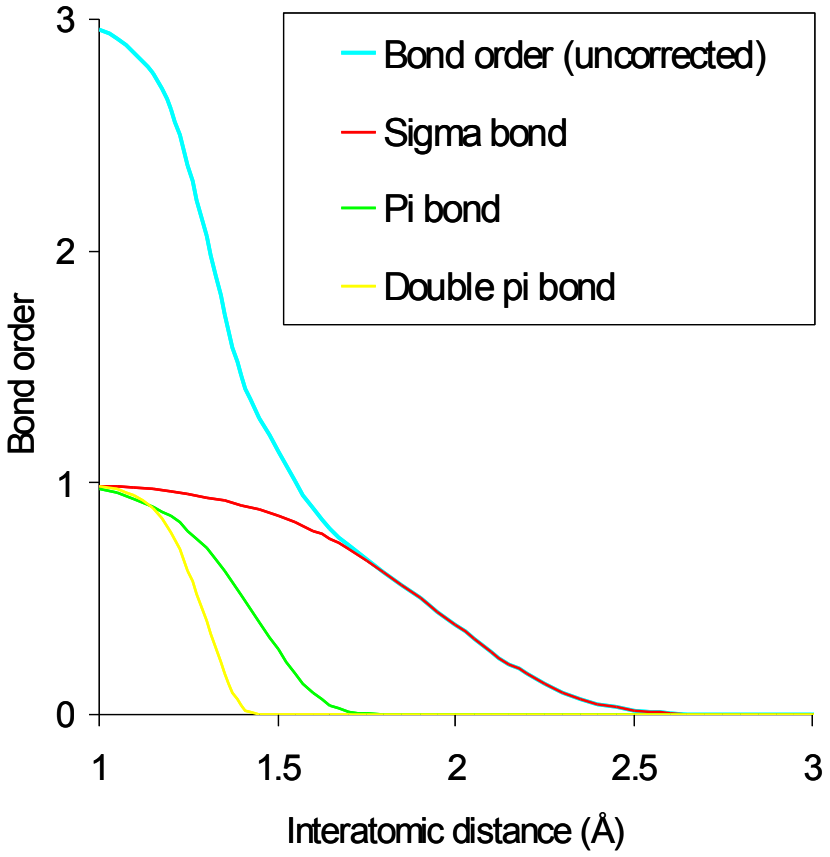
- MD-force field; no discontinuities in energy or forces even during reactions.

- 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

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



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

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

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

.....

.....

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

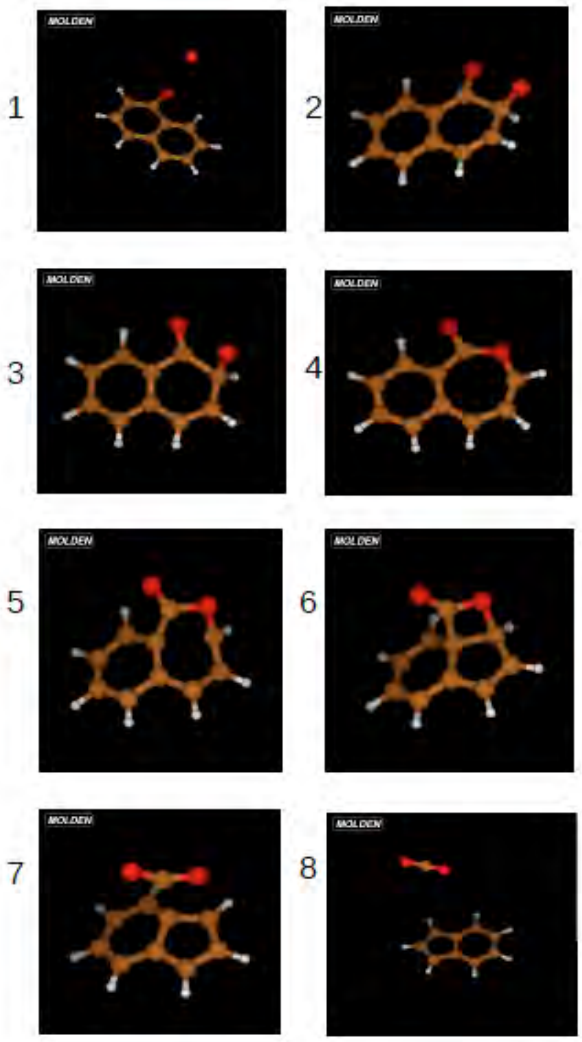
$$\sum_{i=1}^{n} q_i = 0$$

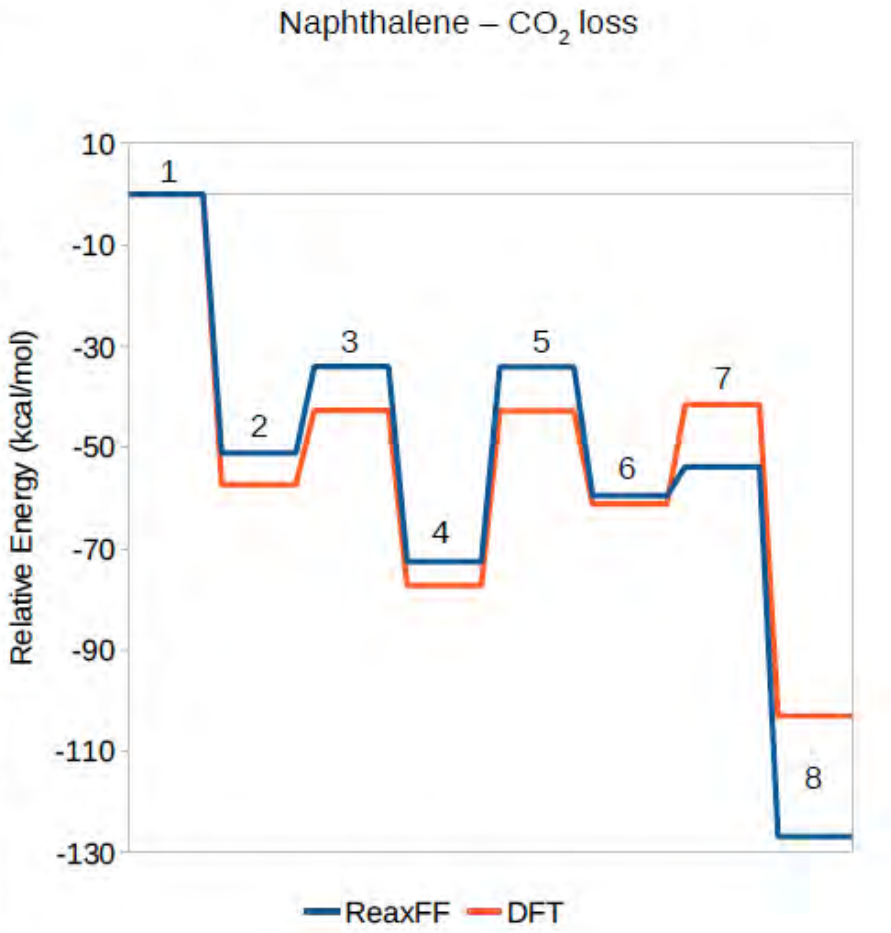
EEM-method
(Mortier et al., JACS 1986);
shielding: Janssens et al. J.Phys.Chem. 1995.

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

χ: atom electronegativity
η: atom hardness
γ: shielding parameter
r: interatomic distances
q:atom charge

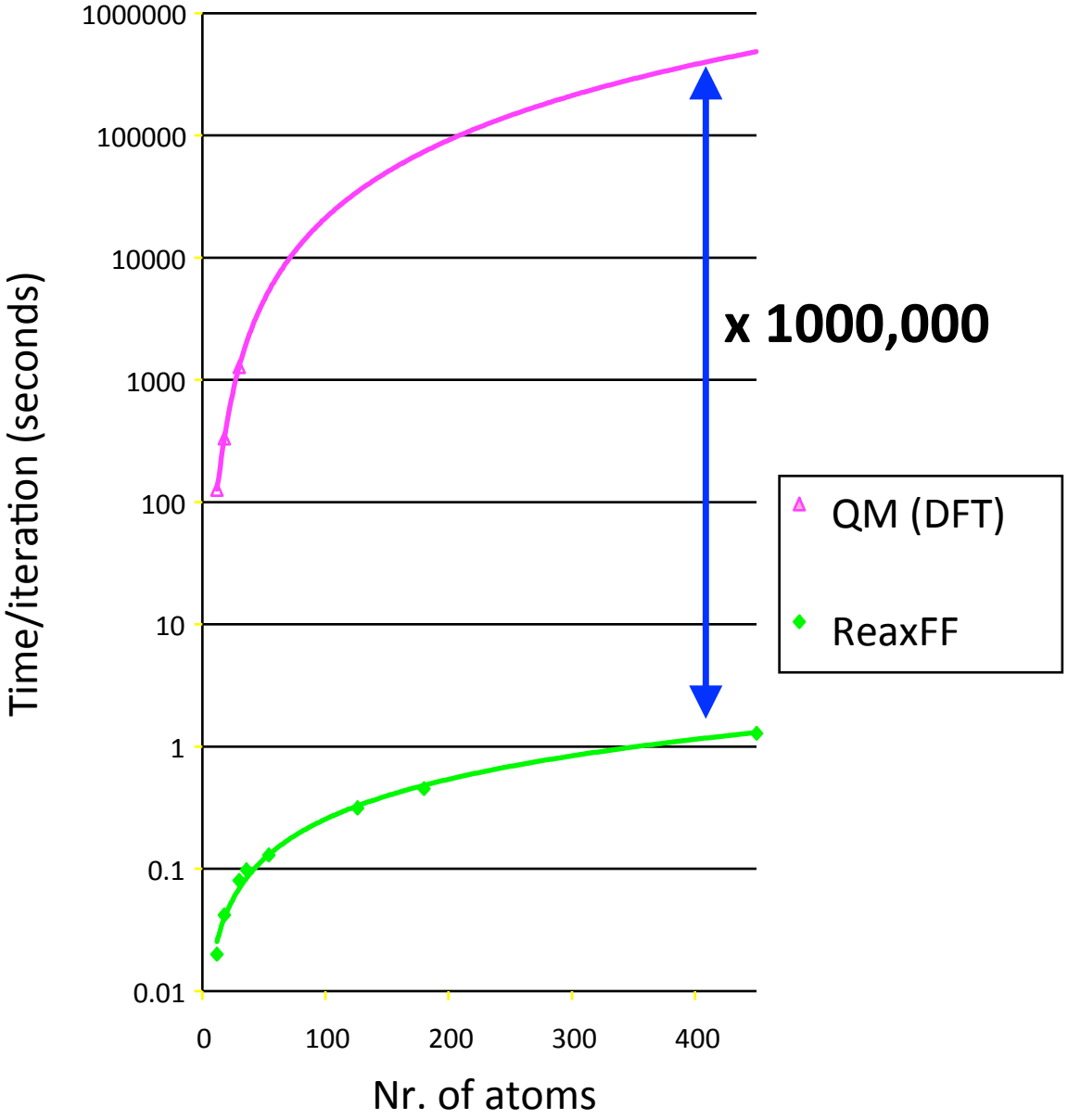
QM/ReaxFF reaction pathways





- Good agreement between ReaxFF and DFT for entire reaction path
- ReaxFF/CHO description (Chenoweth et al. JPC-A 2008) was not specifically fitted to these DFT data

ReaxFF Computational expense



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

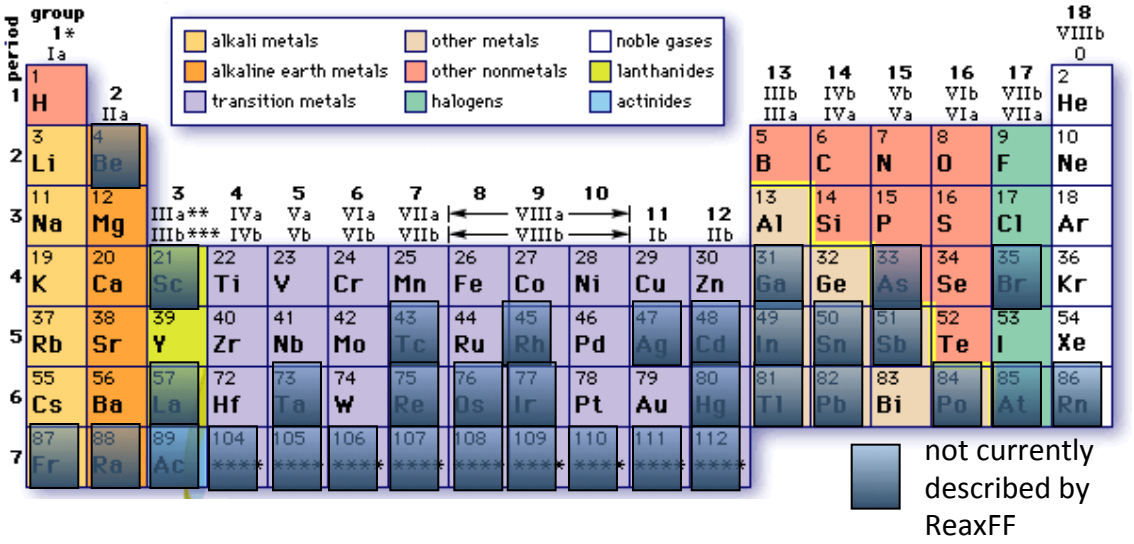
- ReaxFF is 10-50 times slower than non-reactive force fields

- 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 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

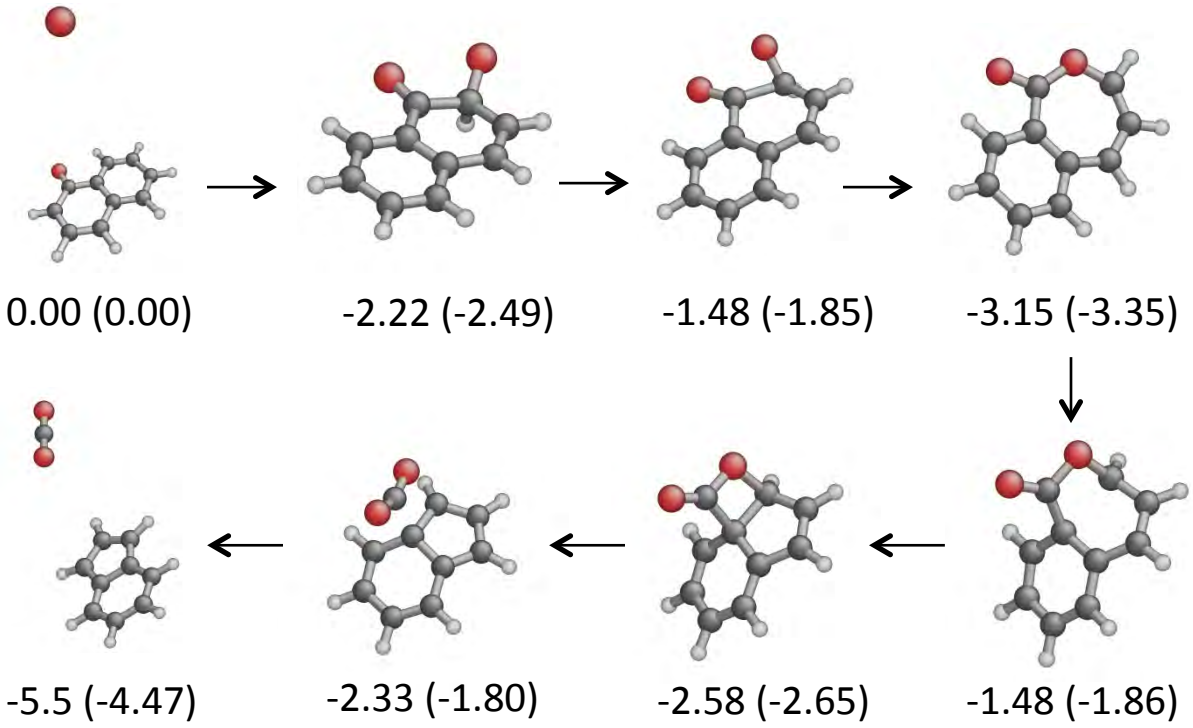
ReaxFF transferability



Graphene oxidation simulations

With Sriram Srinivasan and Tom Schwartzentruber

1. Force field development

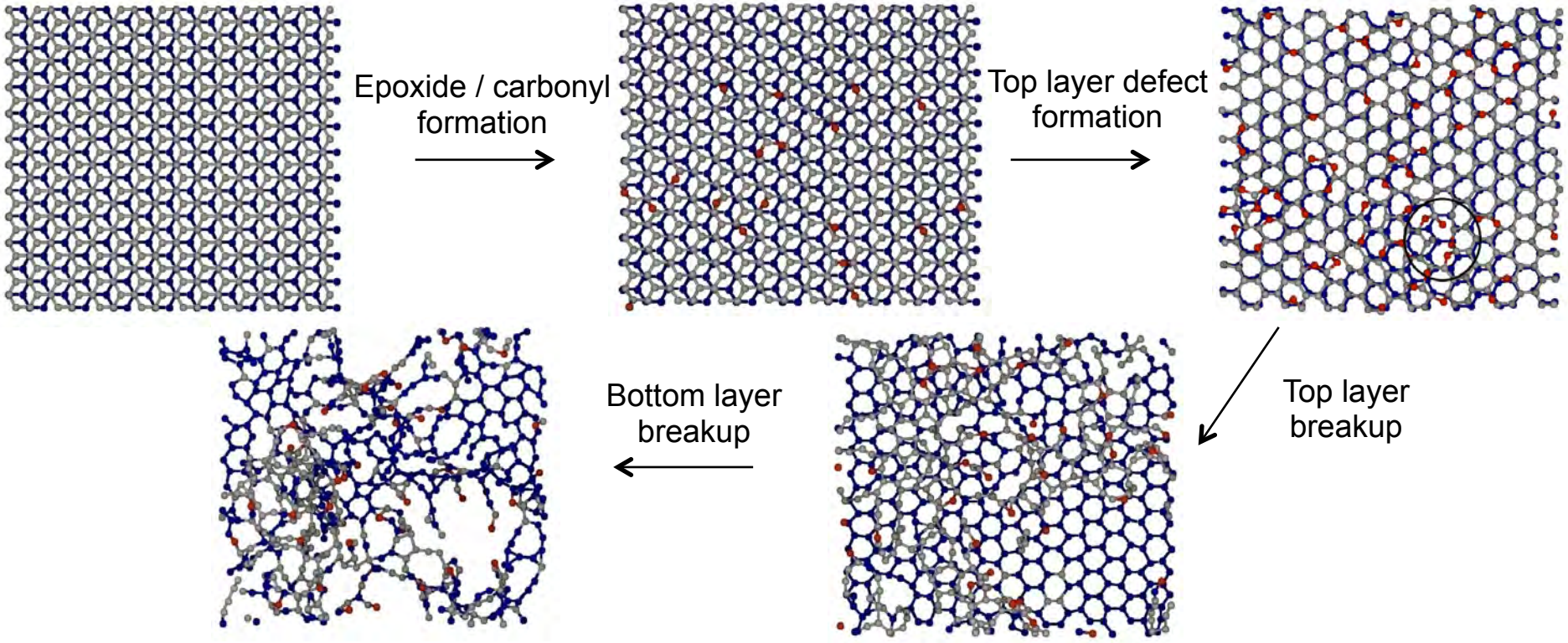


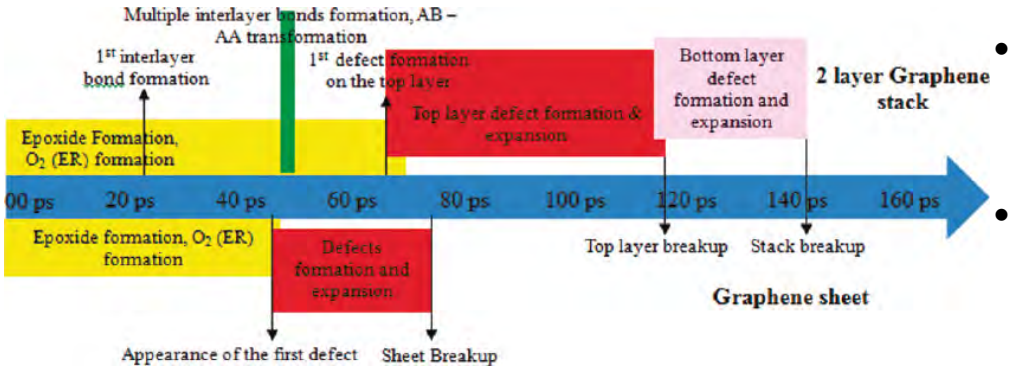
dE in eV/mol;
DFT [2] results in brackets

[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

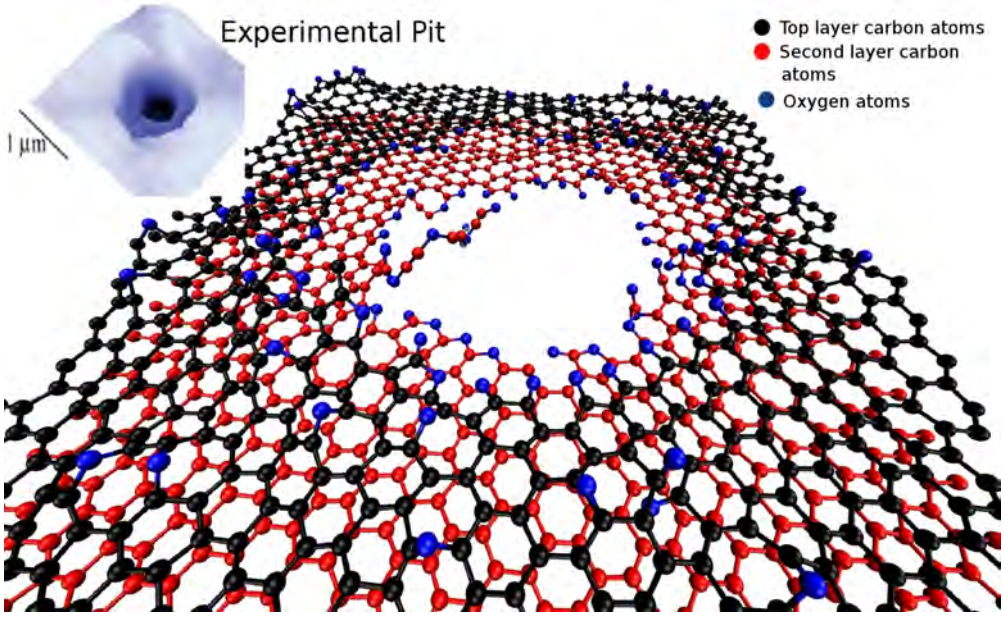


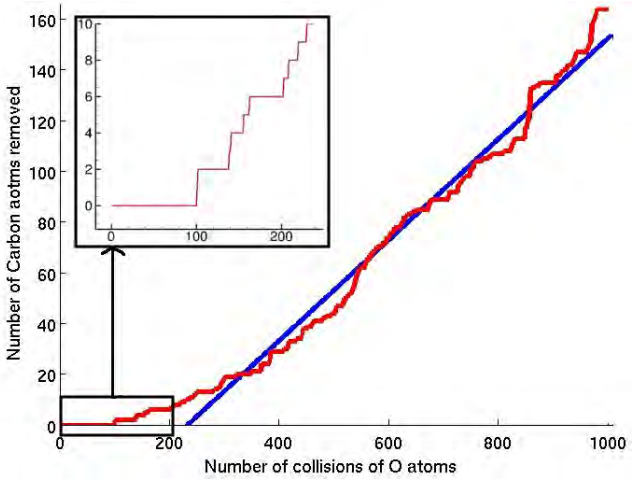


- Results are in good agreeement with DFT/MD simulations (Paci et al.JPC 2009) for 24-atom graphene sheets
- For larger scale systems we observe a distinct different between single-sheet and multi-sheet oxidation kinetics

Goverapet Srinivasan S., van Duin A. C. T., *J. Phys. Chem. A*., **2011**, 115, 13269 – 13280

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





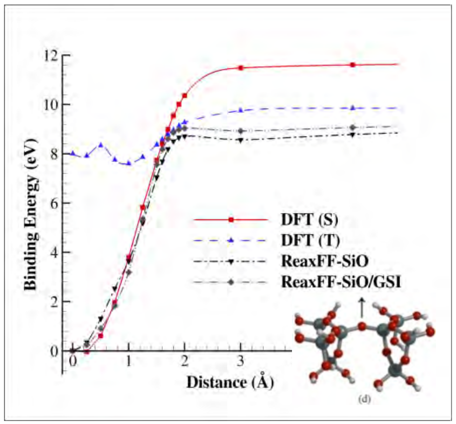
- Molecular beam experiments on HOPG sample showed a pitting behavior. Large shallow pits were observed on the surface of the sample.
- Rate of removal of carbon atoms from the graphite specimen: 1 carbon atom for every 5 oxygen atom collisions

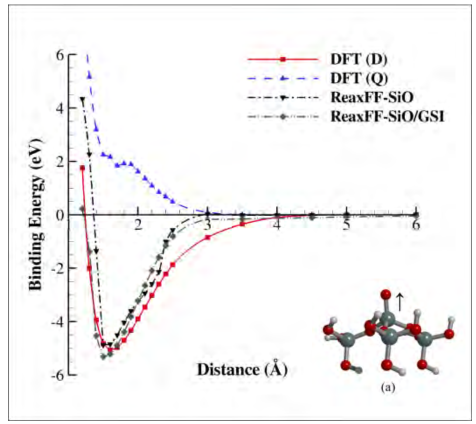
Nicholson K.T., Minton T.K., Seibner S.J., *J. Phys. Chem. B,* **2005,** 109, 8476
Poovathingal S., Schwartzentruber T.E., Goverapet Srinivasan S., van Duin A.C.T., *J. Phys. Chem. C.***2013***,* 117*, 2692*

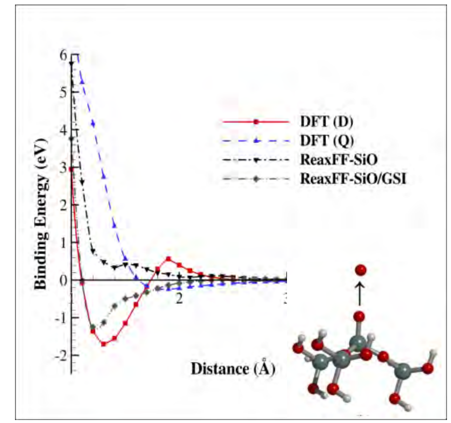
Silica oxidation simulations

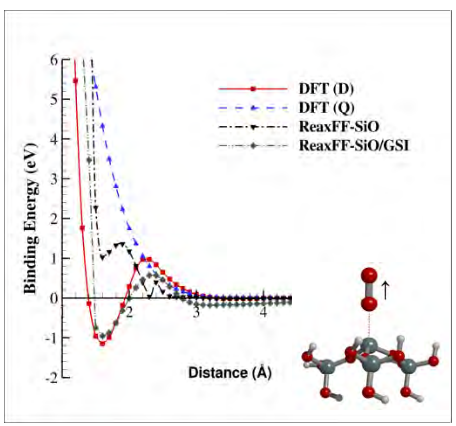
With Sriram Srinivasan, Don Truhlar (U.Minn) and Tom Schwartzentruber (U. Minn)

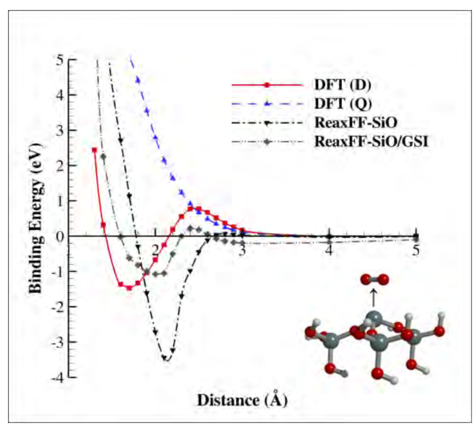
- ReaxFF$_{SiO}$ was re-parameterized against DFT data to obtain a new potential that can accurately model O-silica gas surface interactions.

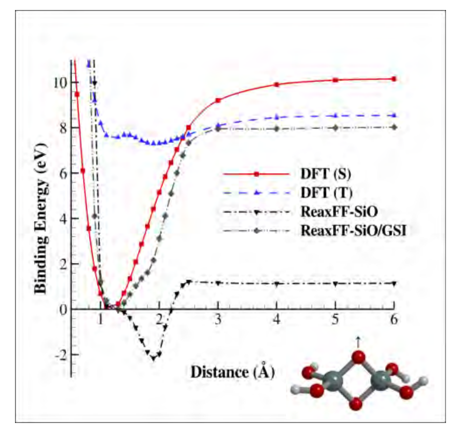






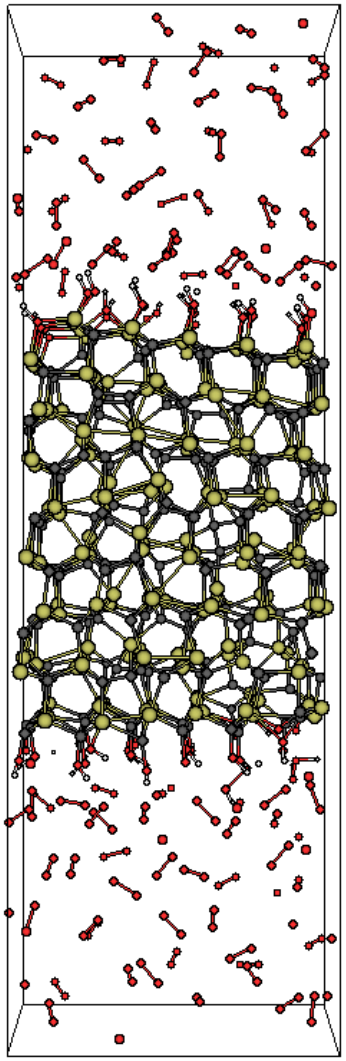






Kulkarni et al, *J. Phys. Chem. C*, **2013,** 117, 258 – 269

Increasing complexity: Silicon carbide oxidation [1,2]



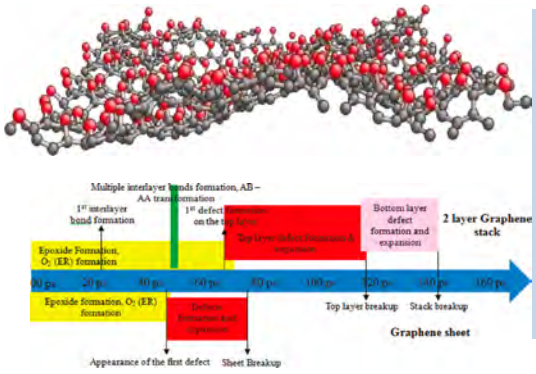
ReaxFF MD simulation of the oxidation of a SiC-slab at T=3000K

- Oxidation of a SiC-slab results in the formation of a protecting SiO_2 layer and a simultaneous phase separation, results in the formation of an amorphous graphitic phase
- Gas phase contains early carbon oxidation products (CO, CO_2), but graphitic phase remains unoxidized for the duration of the MD-simulations

[1] Newsome, D., Sengupta, D., and van Duin, A.C.T. Journal of Physical Chemistry C **2013**, *117*. 5014-5027.
[2] Newsome, D., Sengupta, D., Foroutan, H., Russo, M. F., and van Duin, A. C.T. Journal of Physical Chemistry **2012**, *116*, 16111-16121.

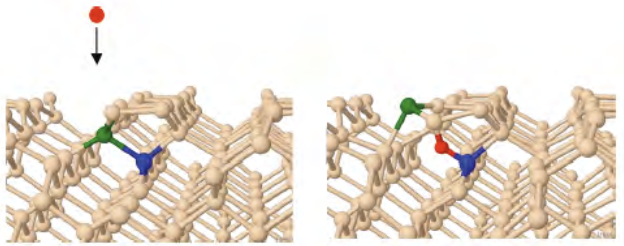
Overview of published work quoting AFOSR/MURI support

Srinivasan, S. G. and van Duin, A. C. T., **2011**. *A molecular dynamics based study of the collisions of hyperthermal atomic oxygen with graphene using the ReaxFF reactive force field.* Journal of Physical Chemistry A **115**, 13269-13280



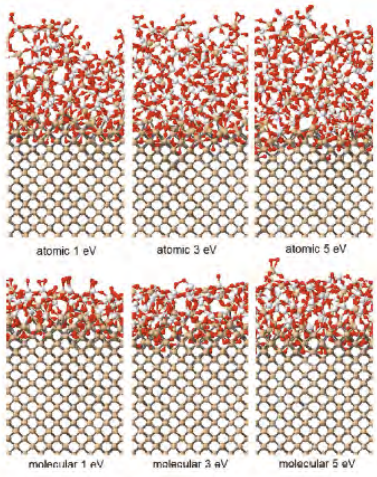
- Identified good general agreement between ReaxFF and DFT for O/ graphene reactions
- Demonstrated detailed kinetics for single- and multi-sheet graphene oxidation

Neyts, E. C., Khalilov, U., Portois, G., and van Duin, A. C. T., **2011**. *Hyperthermal Oxygen Interacting with Silicon Surfaces: Adsorption, Implantation and Damage Creation.* Journal of Physical Chemistry C **115**, 4818-4823.



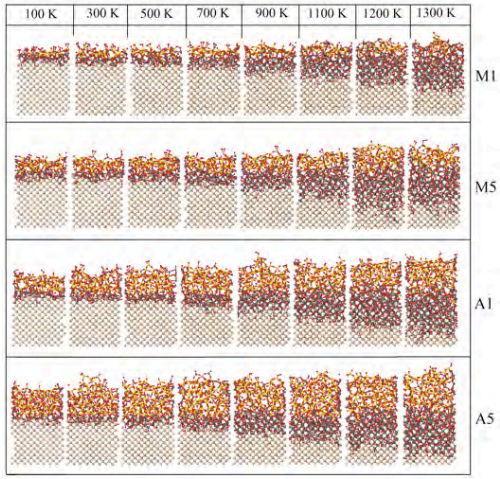
- ReaxFF study of single O-collision events with a Si-surface
- Identified initial binding sites and dominant Si-defect patterns as a function of O-impact velocity

Khalilov, U., Neyts, E. C., Portois, G., and van Duin, A. C. T., **2011**. *Can We Control the Thickness of Ultrathin Silica Layers by Hyperthermal Silicon Oxidation at Room Temperature?* Journal of Physical Chemistry C **115**, 24839-24848.



- Controlled thin-film SiO_2 growth during hyperthermal O-bombardment using ReaxFF
- Found good correlation between oxygen impact velocity and terminal SiO_2 layer thickness

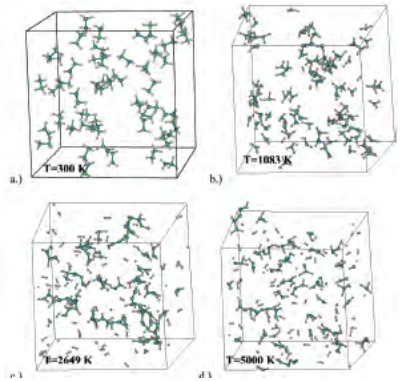
Khalilov, U., Neyts, E. C., Portois, G., and van Duin, A. C. T., **2012**. *Hyperthermal Oxidation of Si(100)2x1 Surfaces: Effect of Growth Temperature*. Journal of Physical Chemistry **116**, 8649-8656



-Thin-film SiO_2 growth during hyperthermal O-bombardment using ReaxFF
- Identified 2 growth mechanisms; low=T and high-T growth
- Transition temperature 700K

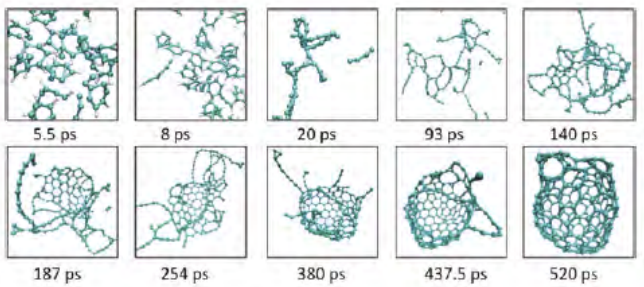
Overview of published work quoting AFOSR/MURI support

Weismiller, M. R., van Duin, A. C. T., Lee, J., and Yetter, R. A., **2010**. *ReaxFF Reactive Force Field Development and Applications for Molecular Dynamics Simulations of Ammonia Borane Dehydrogenation and Combustion*. Journal of Physical Chemistry A **114**, 5485-5492.



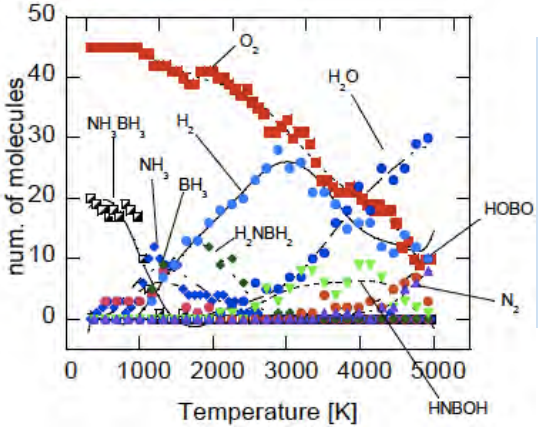
- Developed initial ReaxFF parameters for C/B/N/H compounds
- Provided detailed kinetics for aminoborane dehydrogenation and combustion

Qian, H.-J., van Duin, A. C. T., Morokuma, K., and Irle, S., **2011**. *Reactive Molecular Dynamics Simulation of Fullerene Combustion Synthesis: ReaxFF vs DFTB Potentials*. Journal of Chemical Theory and Computation **7**, 2040-2048.



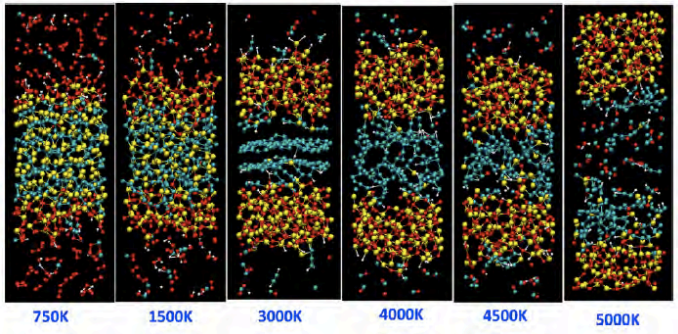
- First ever side-by-side study of DFTB and empirical reactive force fields
- Overall good agreement; found issues with ReaxFF C_3 chemistry which are now resolved (Srinivasan et al., 2012)

Weismiller, M. R., Russo, M. F., van Duin, A. C. T., and Yetter, R. A., **2013**. *Using Molecular Dynamics Simulations with a ReaxFF Reactive Force Field to Develop a Kinetic Mechanism for Ammonia Borane Oxidation*. Proceedings of the Combustion Institute **34,** 3489-3497.



- Detailed study of aminoborane combustion
- Validated ReaxFF B/O description by comparison with experiment and chemical kinetics (CHIMERA) code

Newsome, D., Sengupta, D., Foroutan, H., Russo, M. F., and van Duin, A. C. T., **2012**. *Oxidation of Silicon Carbide by O_2 and H_2O: A ReaxFF Reactive Molecular Dynamics Study:* Part I. Journal of Physical Chemistry **116,** 16111-16121**.**

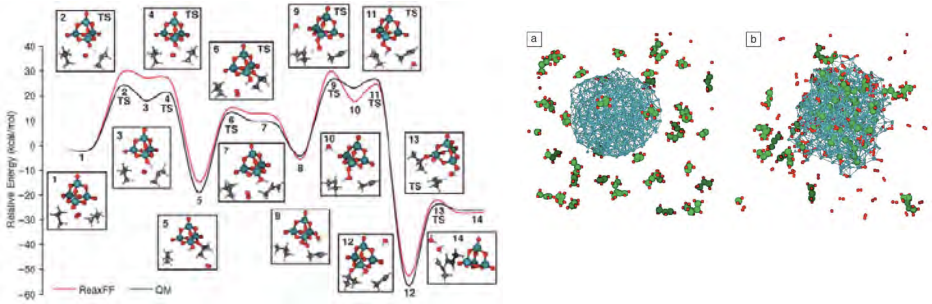


- Study reveals phase-separation of SiC-phase to SiO_2 and graphitic material during high-temperature oxidation
- Detailed kinetic study provided multi-step oxidation mechanism with Arrhenius parameters, enabling integration in mesoscale simulations

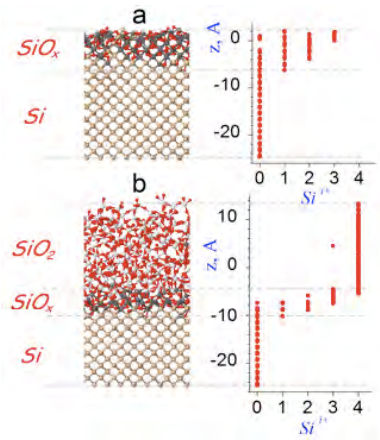
Overview of published work quoting AFOSR/MURI support

Shin, Y. K., Shan, T.-R., Liang, T., Noordhoek, M. J., Sinnot, S. B., van Duin, A. C. T., and Phillpot, S. R., **2012**. *Variable Charge Many-Body Interatomic Potentials*. MRS review **37**, 504-512.

- Overview of state-of-the-art reactive force fields, including ReaxFF and COMB

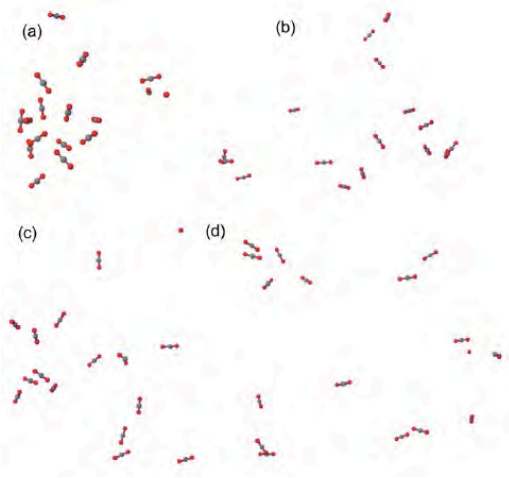


Khalilov, U., Pourtois, G., van Duin, A., and Neyts, E. C., 2012. *Atomic Scale Study of the Si|SiO_2 Interface in Hyperthermal Si Oxidation at Room Temperature.* Chemistry of Materials, **accepted for publication.**



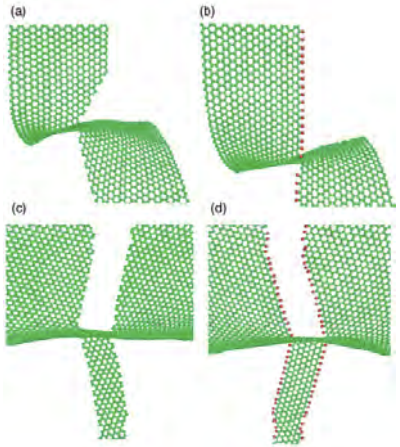
- Detailed ReaxFF study of the formation of suboxide silica structures related to hyperthermal oxygen bombardment on silicon surfaces

Kumar, R., Li, Z., van Duin, A. C. T., and Levin, D., **2011**. *Molecular Dynamics Studies to Understand the Mechanism of Heat Accommodation in Homogeneous Condensing Flow of Carbon dioxide.* Journal of Chemical Physics **135**, 064503.



- Supported by AFOSR/ F49620-02-1-0104
- Provides communication strategies between molecular dynamics and DSMC methods

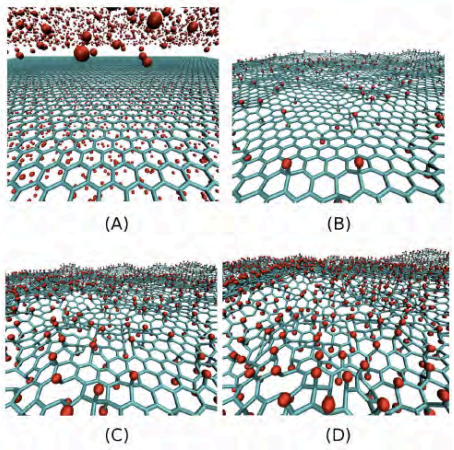
Huang, X., van Duin, A., and Zhang, S., **2012**. *Chemomechanics Origins of Crack Kinking in Graphene*. Physical Review B **85**, 195453/1 - 195453/6.



- ReaxFF study on the dynamics of graphene tearing in different chemical environments
- Demonstrated a significant different between graphene tearing in an oxidizing atmosphere compared to a reducing atmosphere

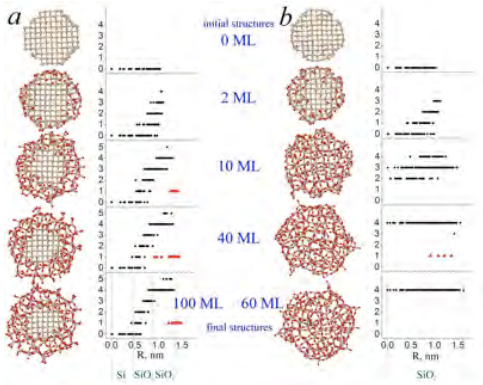
Overview of published work quoting AFOSR/MURI support

R. dos Santos, P. Autreto, S. Legoas, S. Srinivasan, A. van Duin, and D. Galvão, *Graphene to Fluorographene and Fluorographane: A Theoretical Study,* Nanotechnology **24**, 035706



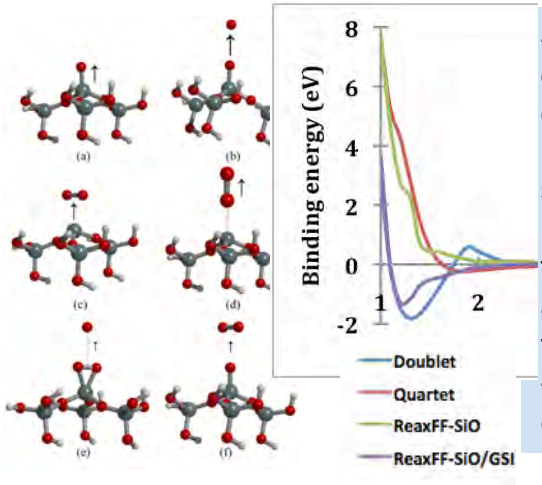
- Study of nanopatterning of fluorine on graphene
- Good agreement between ReaxFF and agreement
- Demonstrates that ReaxFF can reproduce directional effects of graphene substitution, relevant for O/hypergolic studies

U. Khalilov, G. Pourtois, A. Bogaerts, A. C. T. van Duin and E. C. Neyts, *Reactive Molecular Dynamics Simulations on SiO_2-Coated Ultra-Small Si-Nanowires*. Nanoscale **5**, 719-725



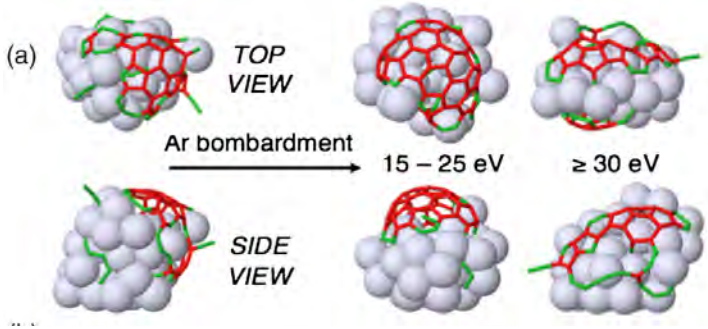
- Study of influence of curvature on Si-nanowire oxidation
- Reveals methodology to control the exact morphology of the nanowire after oxidation
- Significant impact on nanoelectronics development

Kulkarni, A. D., Truhlar, D. G., Srinivasan, S. G., van Duin, A. C. T., Norman, P., and Schwartzentruber, T. E., 2013. *Adsorption of Oxygen on a Quartz Surface: Density Functional Investigation for the Development of a New ReaxFF Force Field,* Journal of Physical Chemistry **117**, 258,-269.



- Systematic improvement of the ReaxFF Si/O description by harvesting relevant SiO_2/O surface structures from high-T ReaxFF MD-studies, followed by DFT-analysis and integration in ReaxFF training set
- Concept can be extended to any material

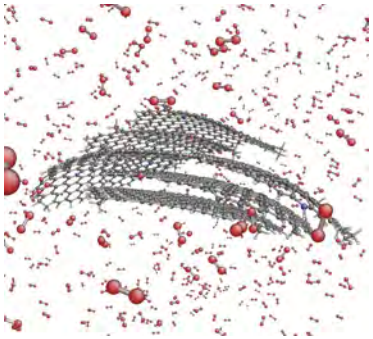
Neyts, E. C., Ostrikov, K., Han, Z. J., Kumar, S., van Duin, A. C. T., and Bogaerts, A., 2013. Defect healing and enhanced nucleation of carbon nanotubes by low-energy ion bombardment. Physical Review Letters **110**, 065501.



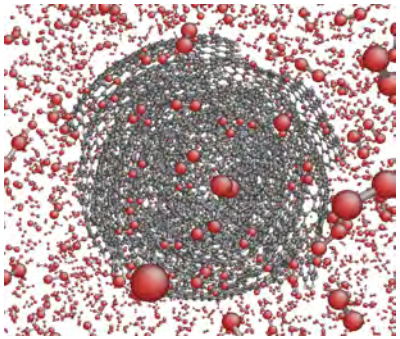
- Combined theory/experiment showing that low-energy Ar-bombardment can help to reduce defect in Ni-catalyzed nanotube growth.
- Demonstrates capability to simulate complex surface chemistry.

Overview of ongoing work

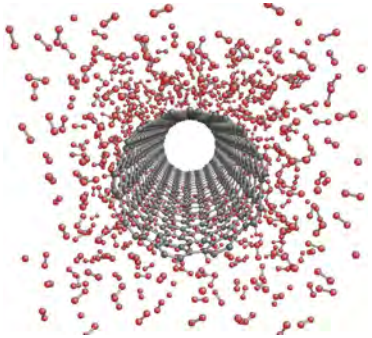
Application to oxidation resistance of various carbon phases



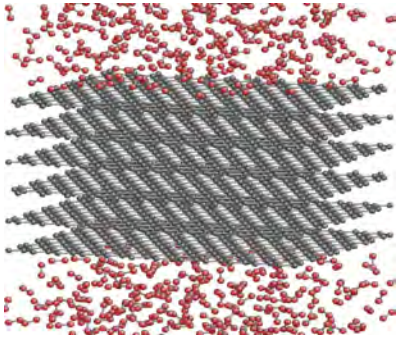
Anthracite



Carbon black



Carbon nanotube



Graphite

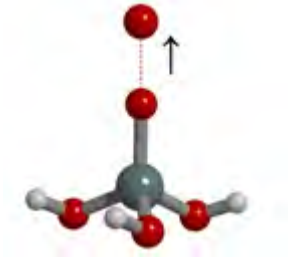
NVT/MD at 3000 K

- Order of reactivity:

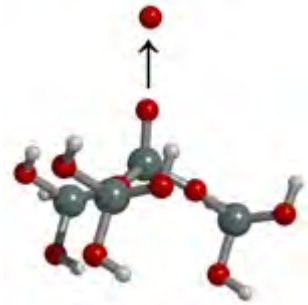
Anthracite > Carbon black > Carbon nanotube > Graphite

- With the present force field description, pristine graphite is inert at 3000 K

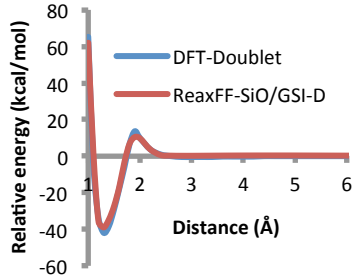
Development of spin dependent force fields to describe oxygen – silica interactions

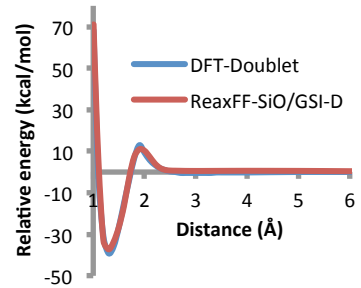


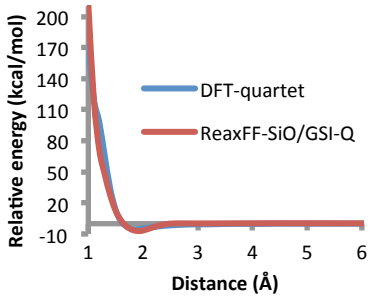
T1-O+O

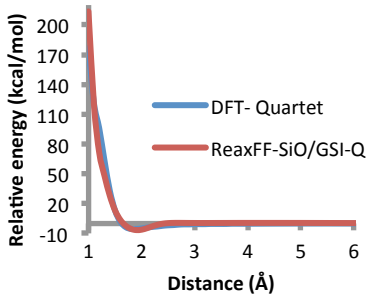


T4-O+O





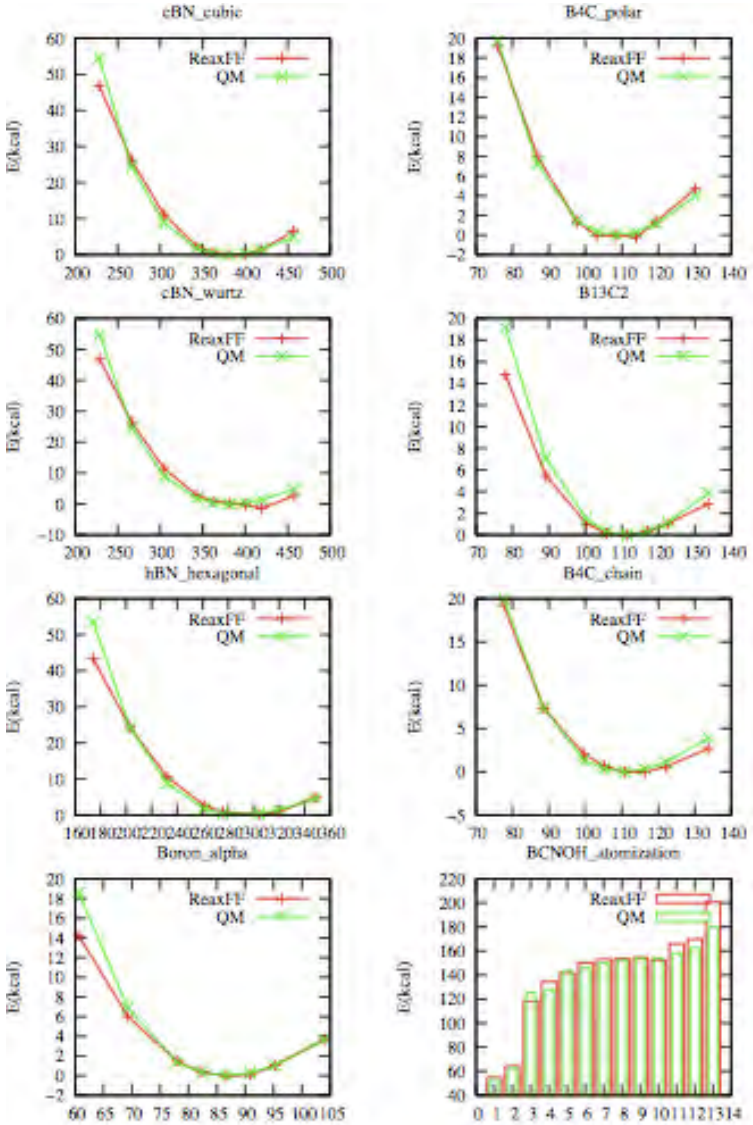




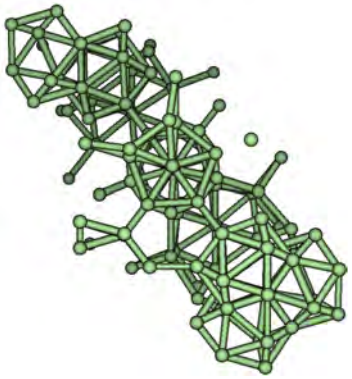
- T1-O+O and T4-O+O were taken as model cases to develop a force field for oxygen interaction that follows a single spin surface

Development of ReaxFF parameters for boron carbides

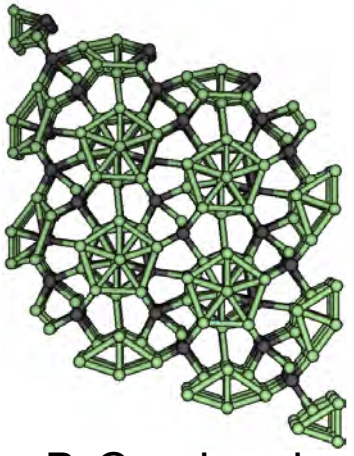
Collaboration with Paulo Branico (IHCP, Singapore)



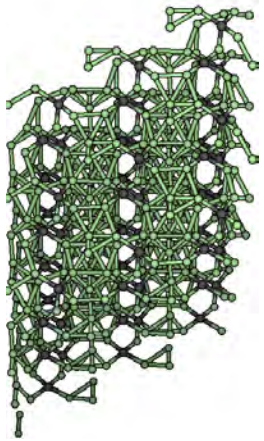
Comparison ReaxFF/QM Equations of State and $E_{atomization}$ for B/C/N condensed phases



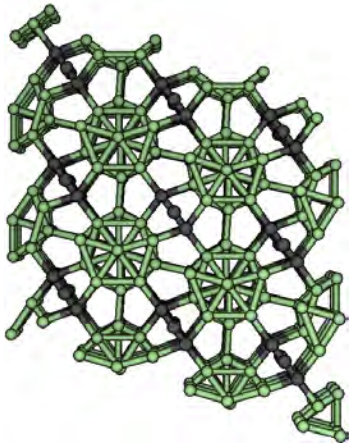
Boron-beta



B_4C-polar phase

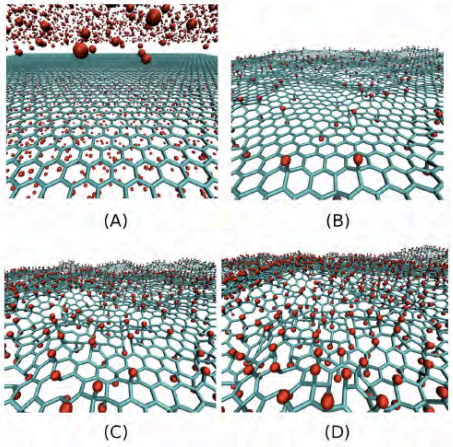


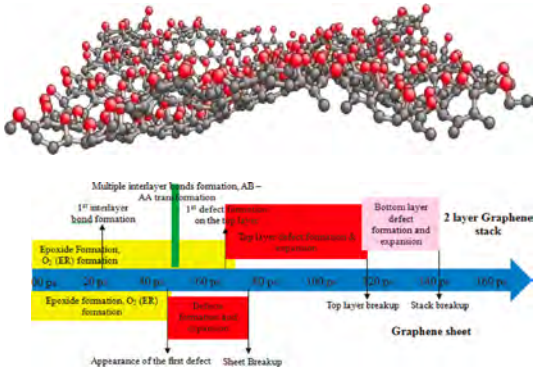
$B_{13}C_2$-phase

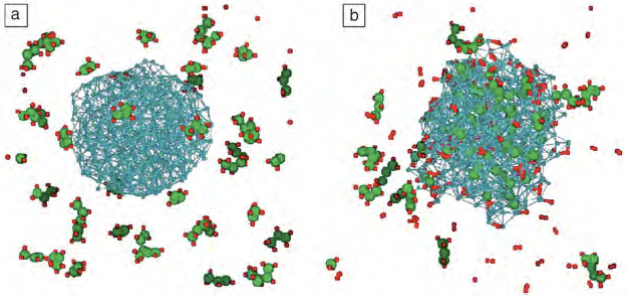


B_4C-chain phase

- ReaxFF can accurately describe the thermodynamics and material behavior of complex boron, boron carbide and boron nitride condensed phases
- Fully integrated with Weismiller et al. B/O/C/N/H and earlier C/H/O/N ReaxFF descriptions







Thank you for your attention