CyberMAGICS Workshop: Reactive Molecular Dynamics

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RMD hands-on: Nitish Baradwaj, Jingxin Zhang, Pranab Sarker, Tyler Zheng

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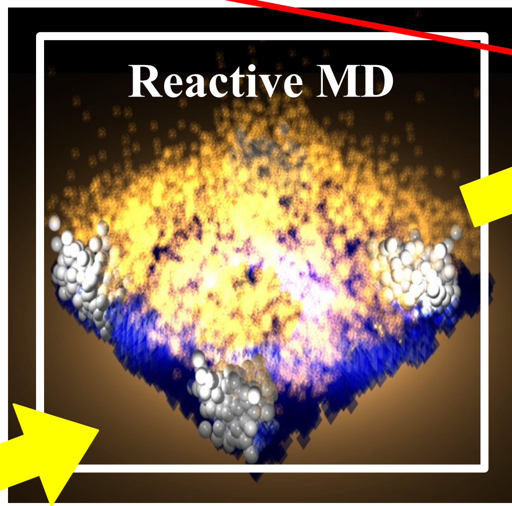
Hierarchy of Molecular Dynamics Methods

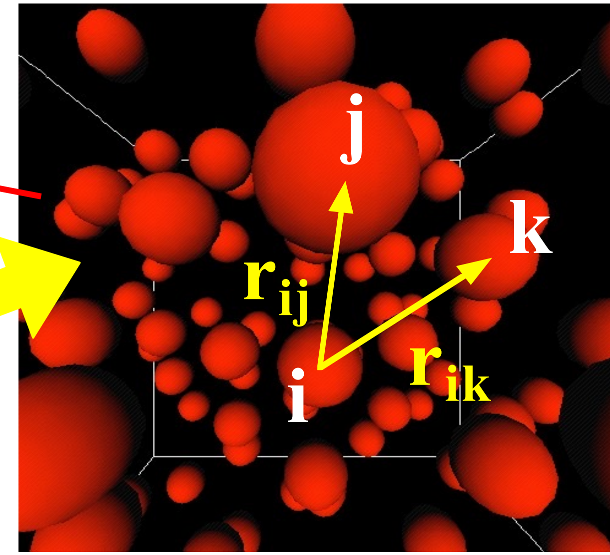
$$m_i \frac{d^2\mathbf{r}_i}{dt^2} = -\frac{\partial}{\partial \mathbf{r}_i} E_{\mathrm{MD}}(\{\mathbf{r}_i\})$$

$$\min E_{\mathrm{QM}}(\{\psi_n(\mathbf{r})\})$$

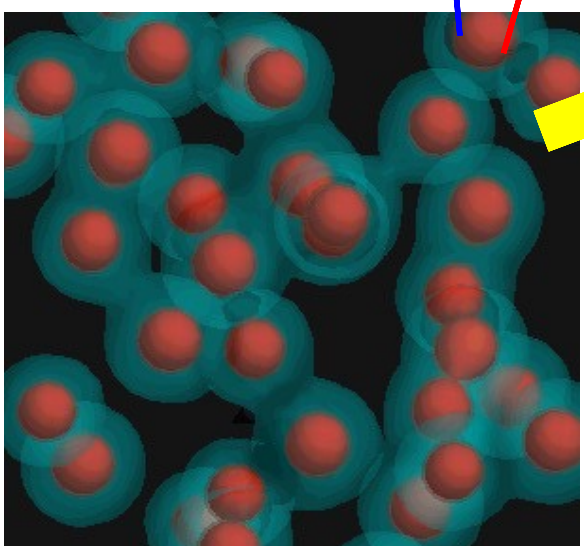
Molecular Dynamics (MD)

Atom





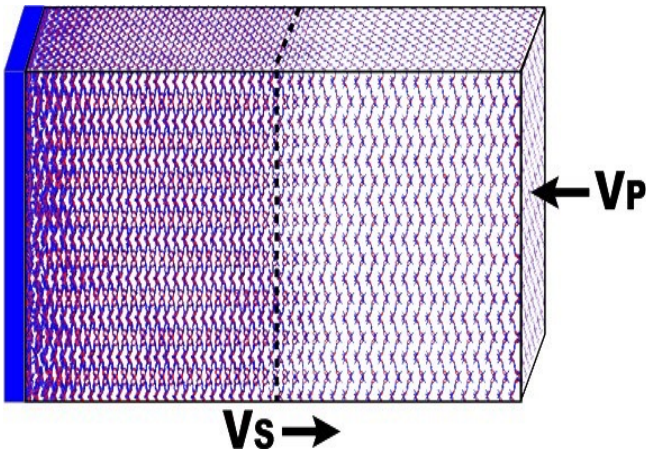
Electron wave function



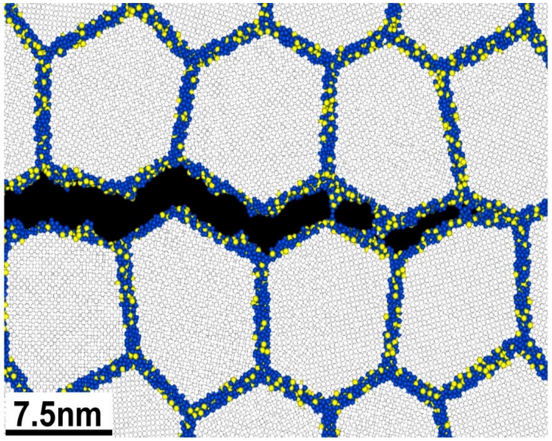
Quantum Mechanics (QM)

- **MD with empirical interactions ~ O(*N*)**
  Long-time (10^9 steps) & large size (10^{12} atoms)
- **DFT quantum MD ~ O(N^3)**
  Short-time (10^4 steps) & small size (~ 400 atoms)
- **Divide-and-Conquer QMD ~ O(*N*)** : Al/Li nanoparticle in water using 16K atoms for 30,000 steps

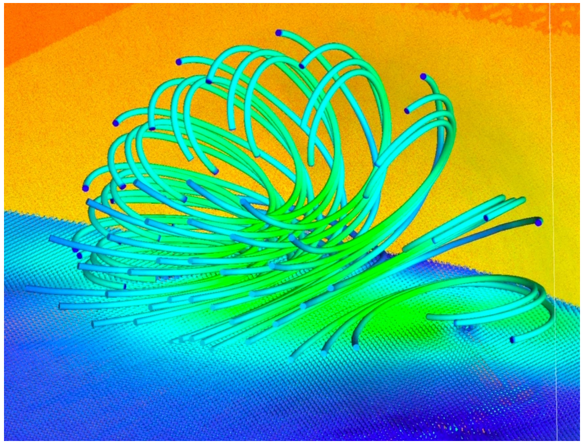
Large-Scale Reactive MD Simulations

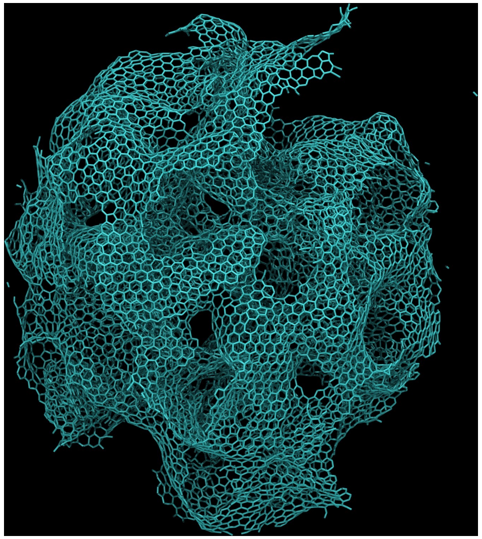


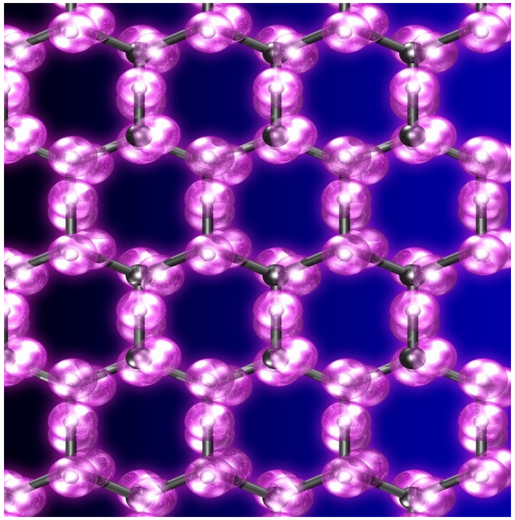
Shock-induced chemical reaction

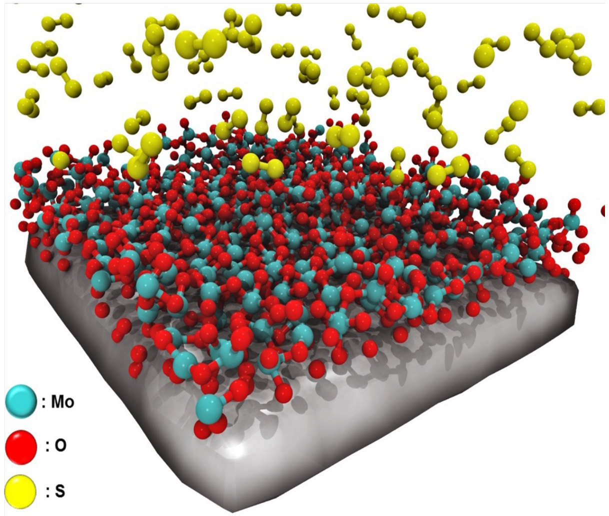


Stress corrosion cracking


Underwater bubble collapse


Oxidation of nanoparticle

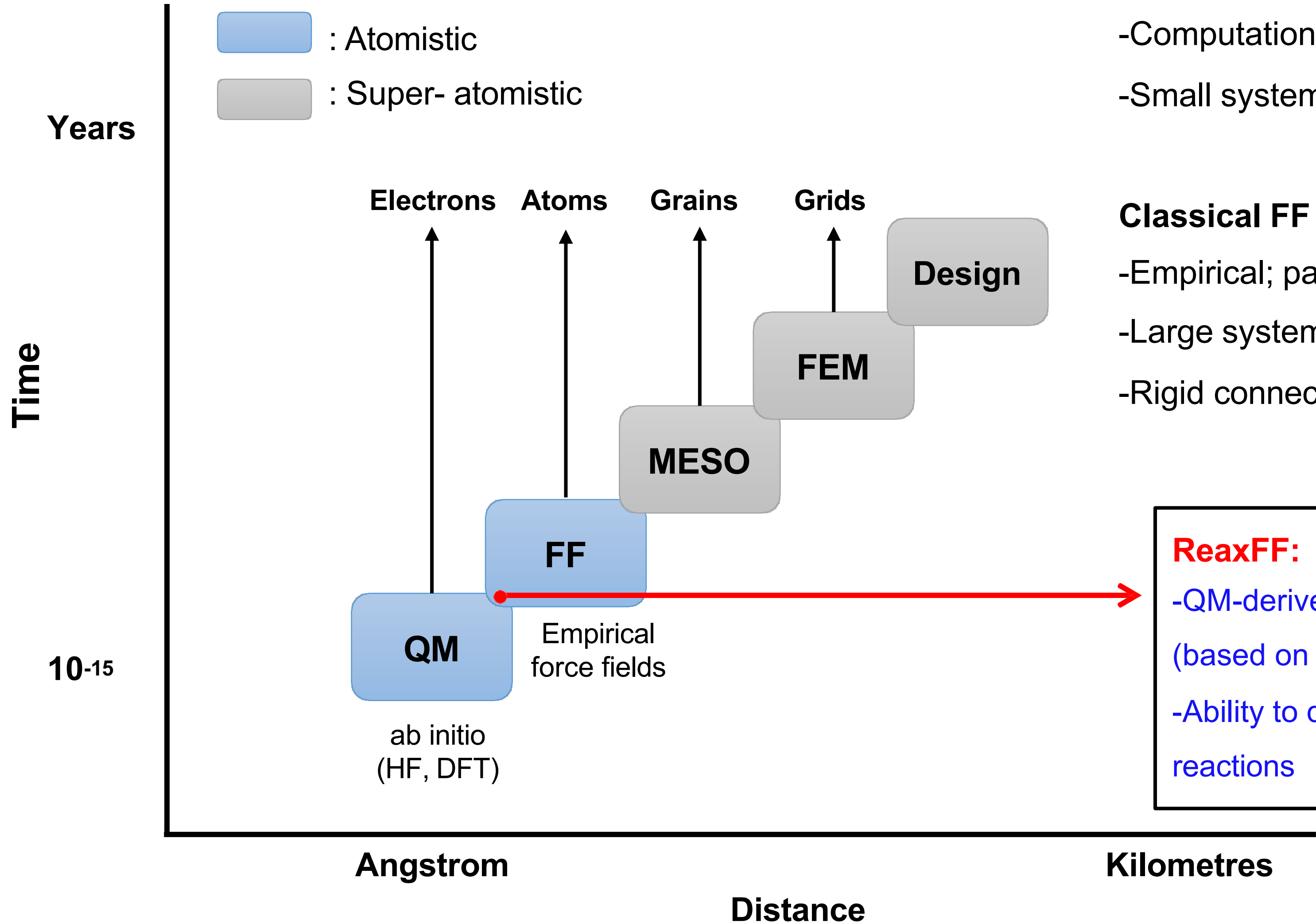

Dielectric polymers



2D material synthesis

Basic Concepts of ReaxFF Forcefield

• Multi-scale Computational Modeling



QM methods:

-Fundamental; electronic level

-Computationally expensive

-Small systems (~100 atoms)

Classical FF methods:

-Empirical; parameters to be trained

-Large systems/high temperatures

-Rigid connectivity

ReaxFF:

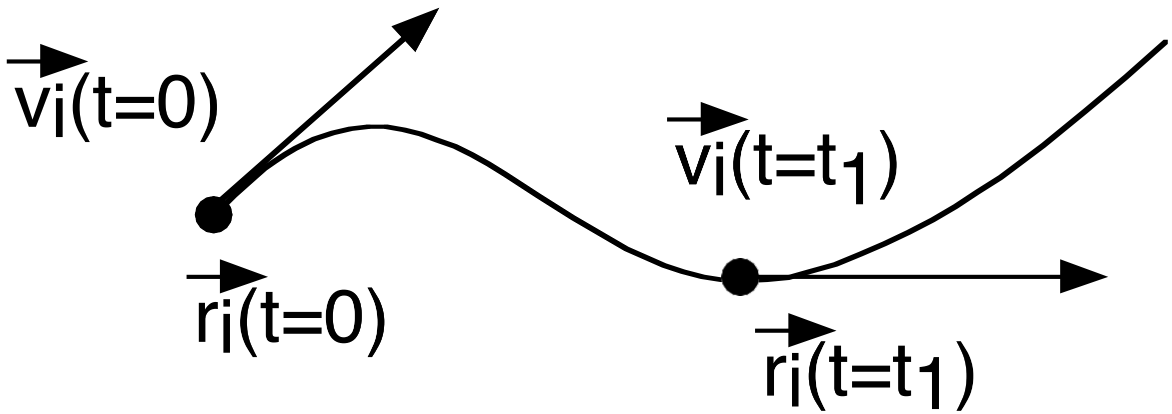
-QM-derived reactive force field

(based on a bond-order scheme)

-Ability to describe chemical reactions

Basic Concepts of ReaxFF Forcefield

- **What is Molecular dynamics (MD) simulation?**



Numerically solve Newton's equation of motion

$$\vec{F}(t) = m\frac{d^2\vec{r_i}}{dt^2} = -\frac{d}{d\vec{r_i}}\boxed{V(\vec{r_i}\,\ldots.\overrightarrow{r_N})}$$

Interatomic potential; force field

Basic Concepts of ReaxFF Forcefield

- **ReaxFF general energy terms***

$$E_{system} = \underbrace{E_{bond} + E_{over} + E_{val} + E_{tors}}_{\text{Bonded interactions}} + \underbrace{E_{vdWaals} + E_{Coulomb}}_{\text{Non-bonded interactions}}$$

E_{bond}: Bond energy; two-body attractive term
E_{over}: Over-coordination energy; penalty for overcoordinating atoms
E_{val}: Angle strain energy; three-body term
E_{tors}: Torsion energy; four-body term

$E_{vdWaals}$: van der Waals interactions
$E_{Coulomb}$: Coulomb interactions

*van Duin, Adri CT, *et al.* *The Journal of Physical Chemistry A* **105** (2001): 9396-9409.

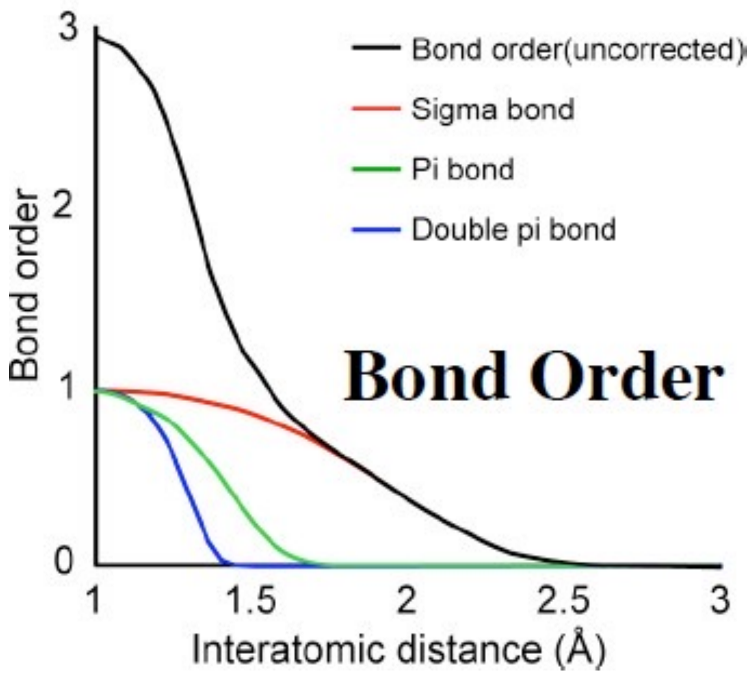
Basic Concepts of ReaxFF Forcefield

- **Key features of ReaxFF – 1***
  - A bond order is calculated and updated every step, thus allowing for chemical reactions during MD simulations.

A bond-order/distance relationship

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

C-C bond order



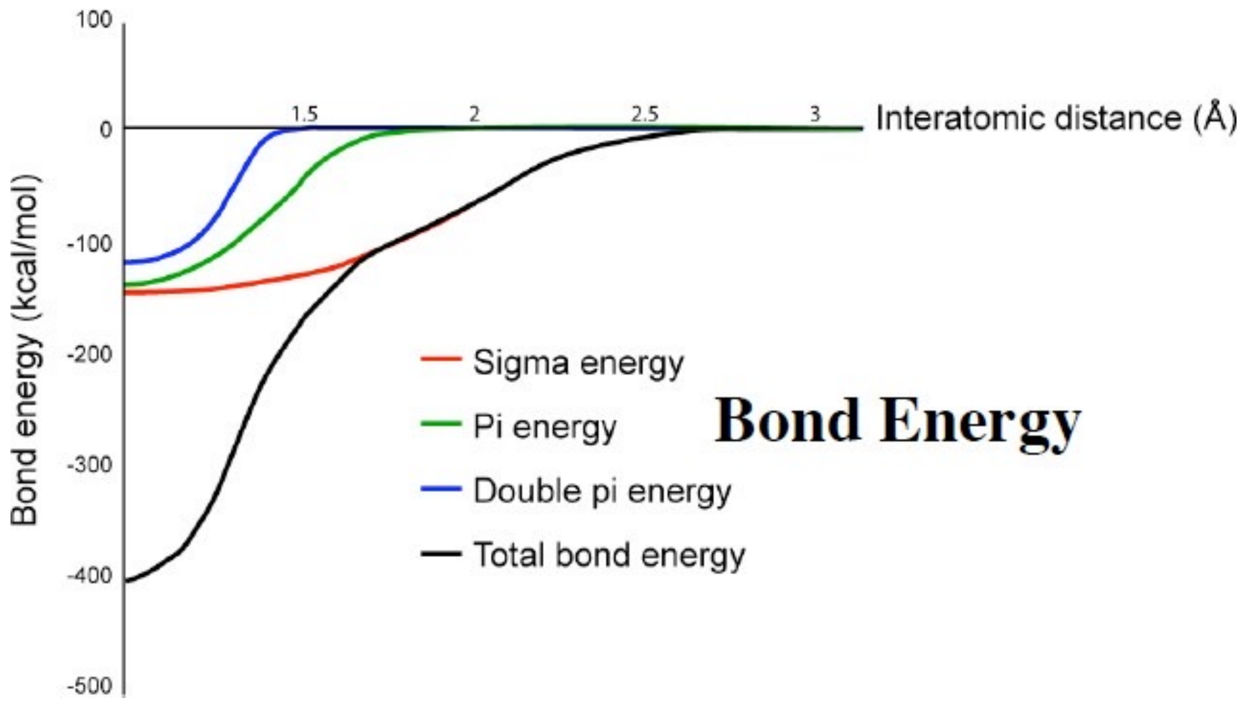
*Russo, Michael F., and Adri CT van Duin. *Nuclear Instruments and Methods in Physics Research Section B: Beam Interactions with Materials and Atoms* **269** (2011): 1549-1554.

Basic Concepts of ReaxFF Forcefield

- **Key features of ReaxFF – 2***

  - All bonded-interactions are made of bond-order dependent.

$$E_{bond} = -D_e^{\sigma} \cdot BO_{ij}^{\sigma} \cdot f(BO_{ij}^{\sigma}) - D_e^{\pi} \cdot BO_{ij}^{\pi} - D_e^{\pi\pi} \cdot BO_{ij}^{\pi\pi}$$



*Russo, Michael F., and van Duin, Adri. *Nuclear Instruments and Methods in Physics Research Section B: Beam Interactions with Materials and Atoms* **269** (2011): 1549-1554.

Basic Concepts of ReaxFF Forcefield

• Key features of ReaxFF – 3*

- Non-bonded interactions (van der Waals and Coulomb) are calculated between every atom pair. (*i.e.*, no exception)
- ReaxFF employs the QEq method,** a geometry-dependent point charge calculations scheme, to update point charges for the entire system.

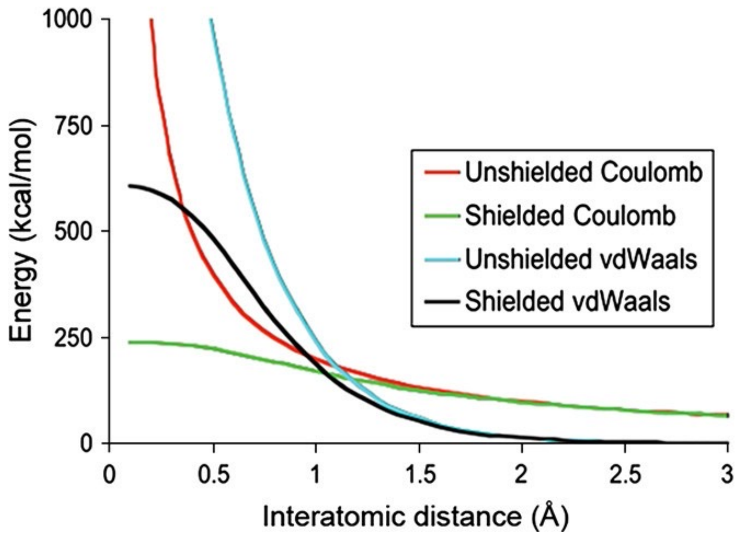
$$E_{vdWaals} = Tap \cdot D_{ij} \cdot \left\{ \exp\left[\alpha_{ij} \cdot \left(1 - \frac{f_{13}(r_{ij})}{r_{vdW}} \right) \right] - 2 \cdot \exp\left[\frac{1}{2} \cdot \alpha_{ij} \cdot \left(1 - \frac{f_{13}(r_{ij})}{r_{vdW}} \right) \right] \right\}$$

A shielded Morse potential

$$f_{13}(r_{ij}) = \left[r_{ij}^{p_{vdW1}} + \left(\frac{1}{\gamma_w} \right)^{p_{vdW1}} \right]^{\frac{1}{p_{vdW1}}}$$

$$E_{\text{Coulomb}} = C \cdot \frac{q_i \cdot q_j}{[r_{ij}^3 + (1/\gamma_{ij})^3]^{1/3}}$$

A shielded Coulomb potential



*.Russo, Michael F., and Adri CT van Duin. *Nuclear Instruments and Methods in Physics Research Section B: Beam Interactions with Materials and Atoms* **269** (2011): 1549-1554.

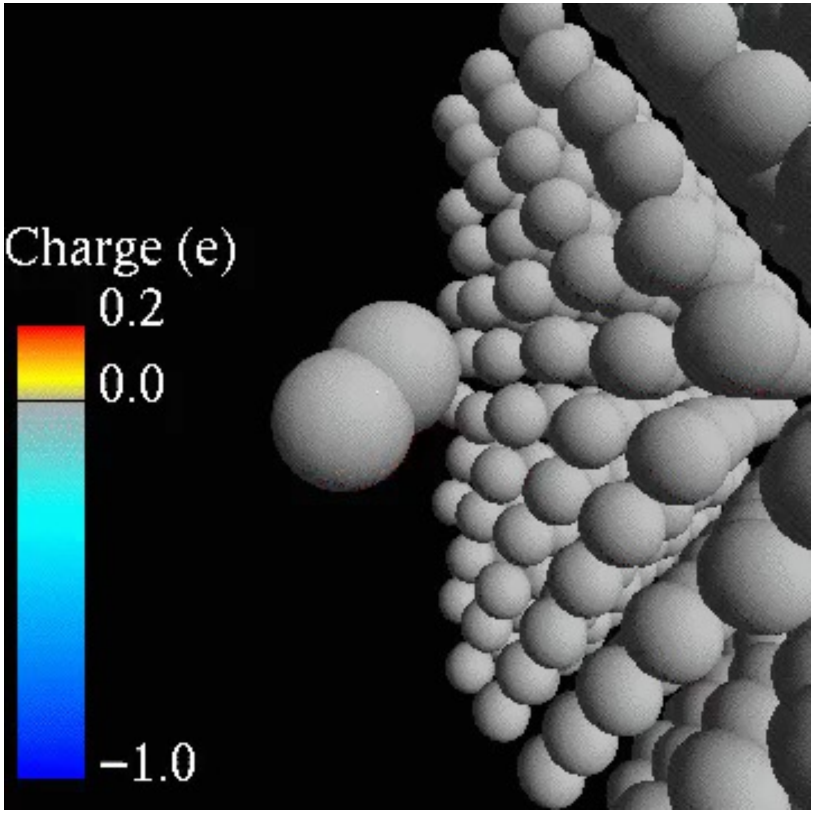
Rappe, Anthony K., and William A. Goddard III. *The Journal of Physical Chemistry* **95 (1991): 3358-3363.

Basic Concepts of ReaxFF Forcefield

Key features of ReaxFF – 4**

- **Charge-equilibration (QEq)**
  → Charge transfer

  Determine atomic charges $\{q_i \mid i = 1, ..., N\}$ every MD step to minimize $E_{\mathrm{ES}}(\mathbf{r}^N, q^N)$ with charge-neutrality constraint: $\Sigma_i\, q_i = 0$

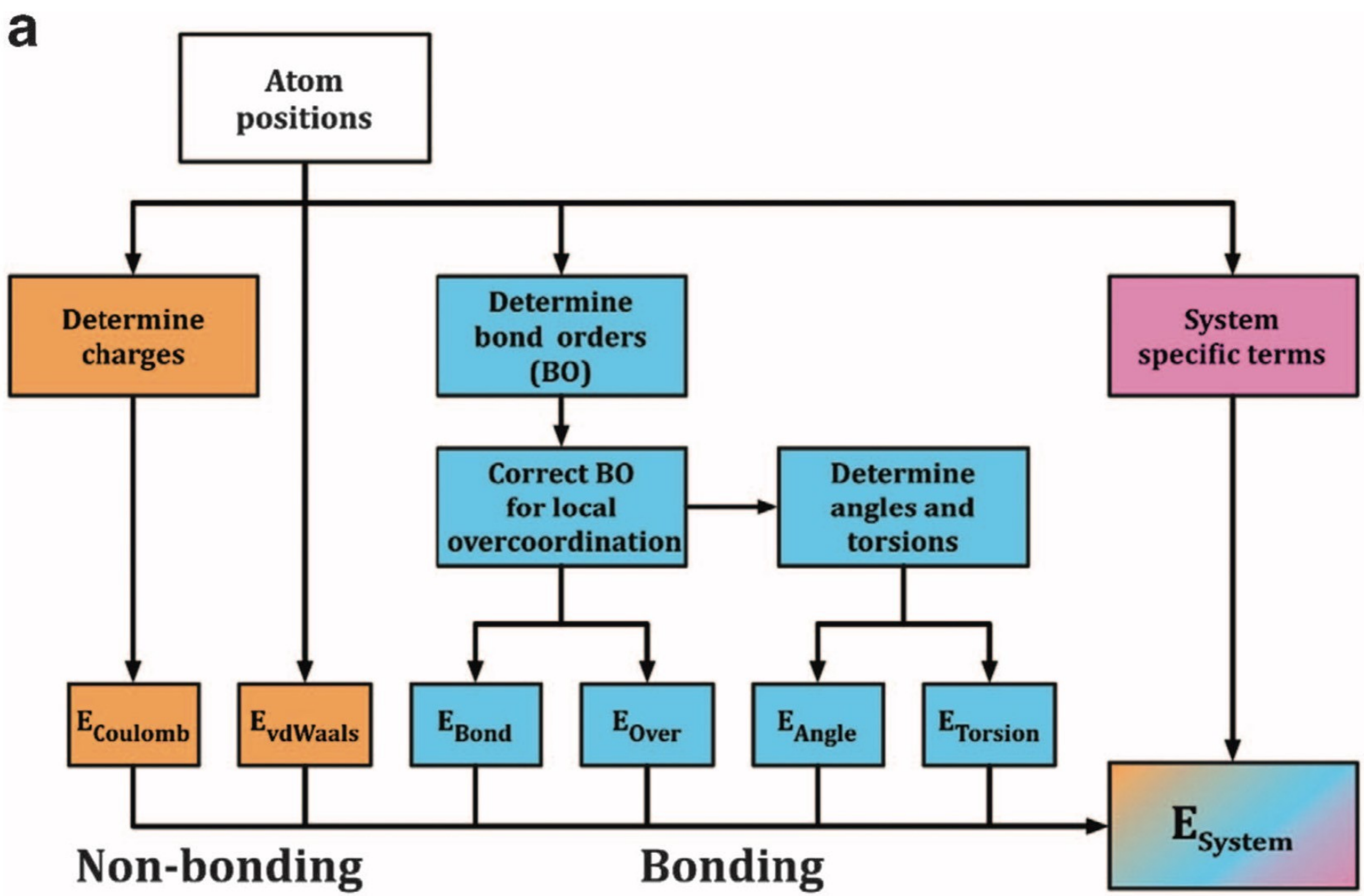


O_2 dissociation on Al(111)

$$E_{\mathrm{ES}}\left(\mathbf{r}^N, q^N\right) = \sum_i \left(\chi_i q_i + \frac{1}{2} J_i q_i^2\right) + \sum_{i<j} \int d\mathbf{x} \int d\mathbf{x}' \frac{\rho_i(q_i; \mathbf{x} - \mathbf{r}_i)\rho_j(q_j; \mathbf{x}' - \mathbf{r}_j)}{|\mathbf{x} - \mathbf{x}'|}$$

Basic Concepts of ReaxFF Forcefield

- **ReaxFF flow diagram***



*Senftle, Thomas, *et al. npj Computational Materials* **2** (2016).

Basic Concepts of ReaxFF Forcefield

- **How to get ReaxFF reactive force field parameters?**
  - **Do search Google Scholar: https://scholar.google.com/**
  - **Develop your ReaxFF force field parameters (non-trivial)**

A Step for the force field training

1. Set up training sets with QM data
2. Optimize ReaxFF parameters using a single-search scheme*
3. Validate the ReaxFF parameters by performing MD simulations of simple systems

Minimize the total error

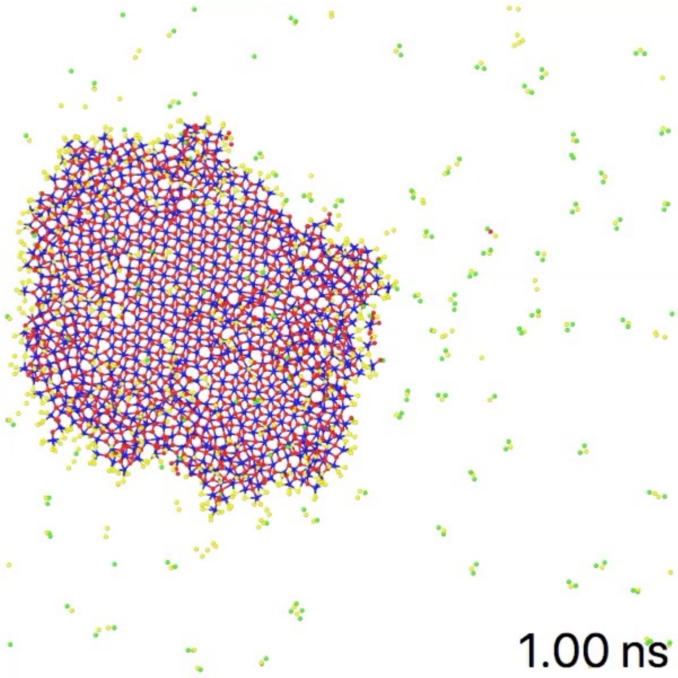
$$\text{Error} = \sum_{i=1}^{n}\left[\frac{\left(x_{i,QM} - x_{i,ReaxFF}\right)}{\sigma}\right]^2$$

* van Duin, A. C. T.; Jan, M.; de Graaf, B. *J. Chem. Soc., Faraday Trans.* **1994,** 90, (19), 2881-2895.

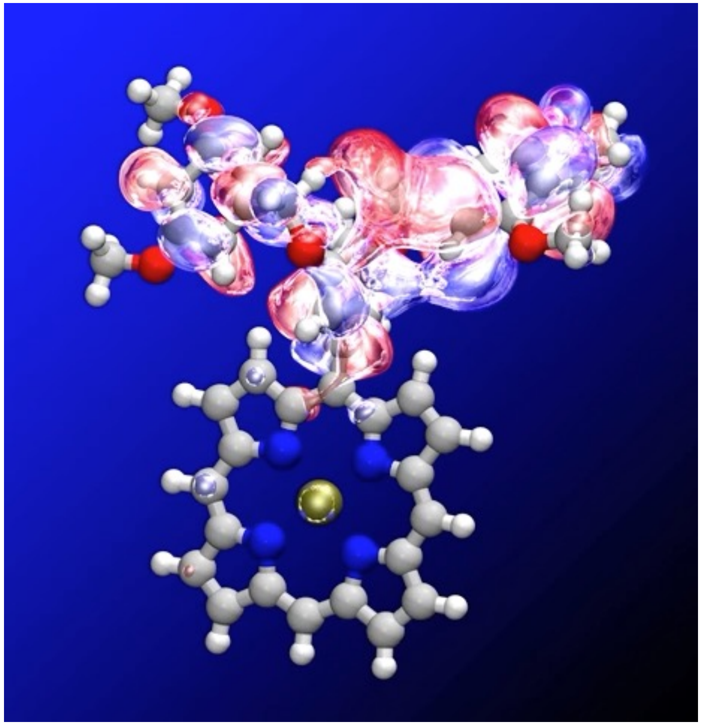
Reactive and Quantum MD Software

RXMD: **Reactive molecular dynamics software for desktop to supercomputing platforms**

QXMD: **Quantum dynamics software with non-adiabatic extensions**



Sulfurdization of MoO_3 nanoflake



Electron transfer in light-harvesting molecule

Extended-Lagrangian Method

- **Eliminated speed-limiting iteration for charge-equilibration (QEq) in ReaxFF by adapting an extended-Lagrangian scheme proposed for QMD**

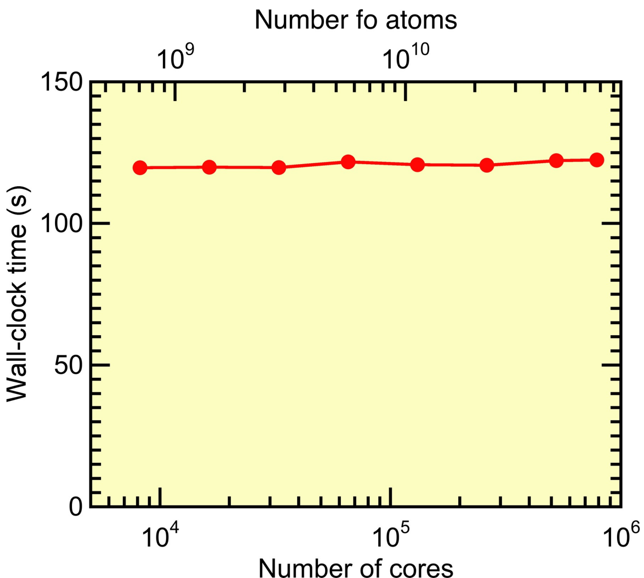
$$L_{\mathrm{XRMD}} = L_{\mathrm{RMD}} + \frac{\mu}{2}\Sigma_i \dot{\theta}_i^2 - \frac{\mu\omega^2}{2}\Sigma_i(\theta_i - q_i)^2$$

Auxiliary charge: dynamic variable

Physical charge

- **Extended-Lagrangian RXMD achieves 8.6x speed up with the same energy conservation as fully converged QEq**

- **Parallel efficiency 0.977 on 786,432 Blue Gene/Q cores for 67.6 billion atoms**

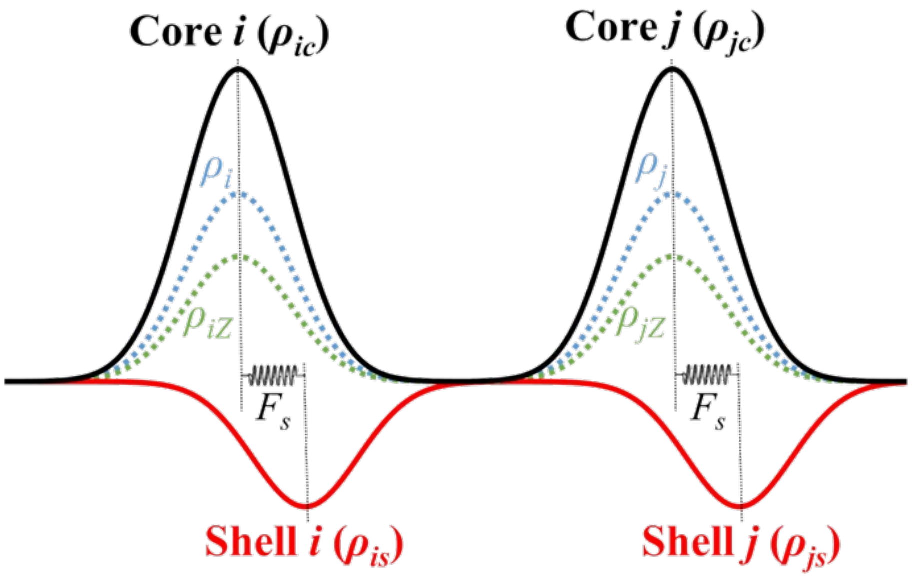


P. Souvatzis & A. Niklasson, *J. Chem. Phys*. **140**, 044117 ('14)
Nomura *et al*., *Comput. Phys. Commun*. **192**, 91 ('15)

Polarizable Charge Equilibration (PQEq) Method

- **PQEq method has been implemented in RXMD to study dielectric response as a function of time, electric field and temperature.**

- **Each atom is partitioned into two charged sites, i.e., core and shell**
- **The core consists of variable charge ρ_i and with fixed charge ρ_{iZ}**
- **The shell is connected with the core by an isotropic harmonic spring with force constant F_s**



self energy of *i*-atom

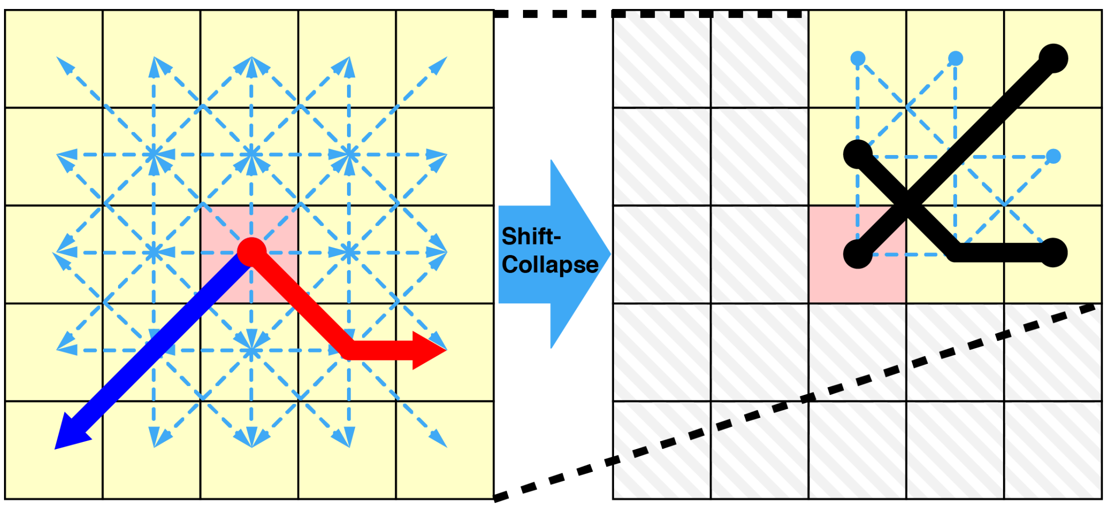
core-shell interaction on *i*-atom

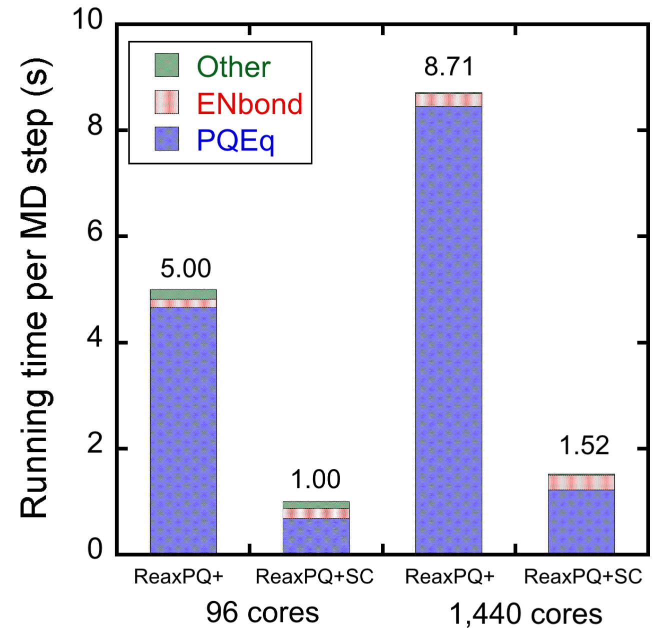
$$E(\{\vec{r}_{ic},\vec{r}_{is},q_i\}) = \sum_i^N \left\{ E_i^0 + \chi_i^0 q_i + \frac{1}{2} J_{ii}^0 q_i^2 + \boxed{\frac{1}{2} K_s r_{ic,is}^2} \right\}$$

$$+ \sum_{i>j} \left[C(\vec{r}_{ic,jc}) q_{ic} q_{jc} - C(\vec{r}_{ic,js}) q_{ic} Z_j - C(\vec{r}_{is,jc}) q_{jc} Z_i + C(\vec{r}_{is,js}) Z_i Z_j \right]$$

core-shell interaction between *i*- and *j*-atoms

Shift-Collapse (SC) Algorithm for Time-to-Solution

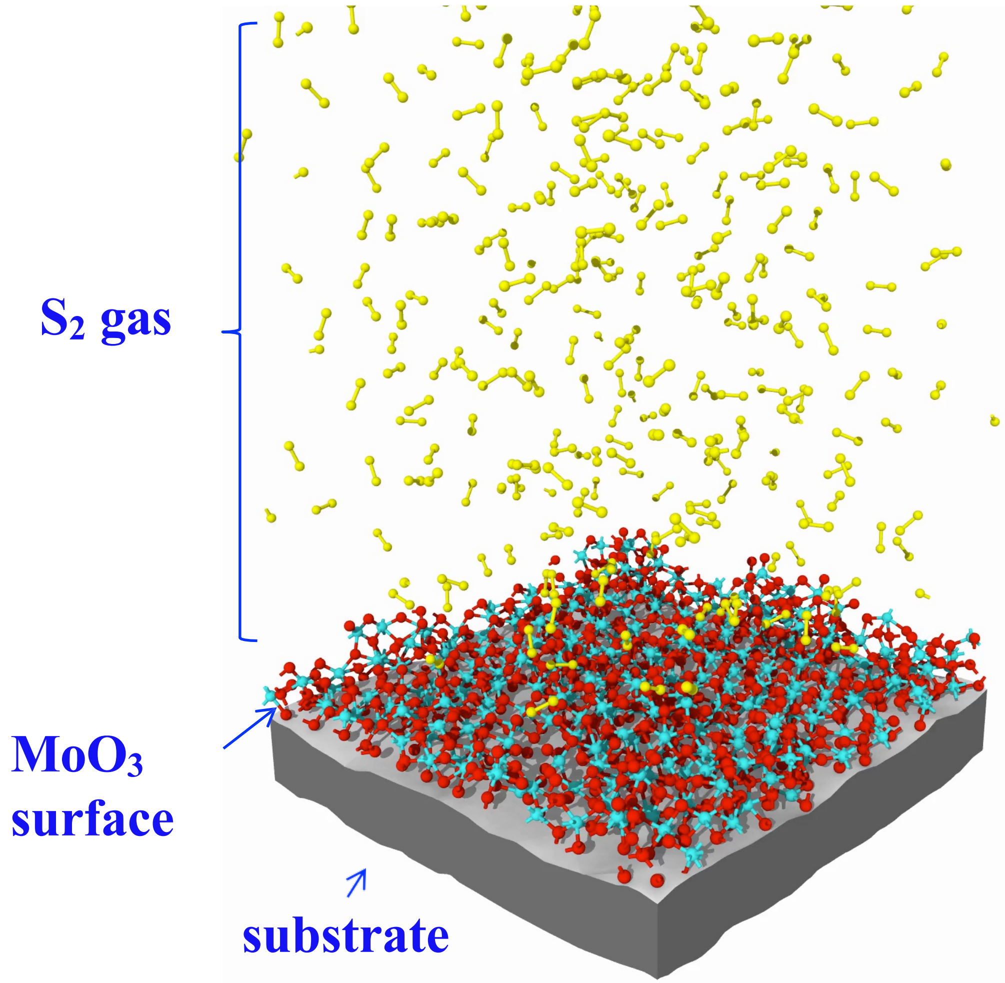




- **SC algorithm generates optimal computation pattern for general finite-range *n*-tuple energy/force computations.**
- **SC-accelerated PQEq+SC achieves 5.0x speedup compare to the original PQEq.**

M. Kunaseth, et al., Proceedings of Supercomputing SC13, 2013
K. Liu, et al. IEEE/ACM 9th Workshop ScalA 2018

RMD Simulations of MoS_2 Monolayer Synthesis



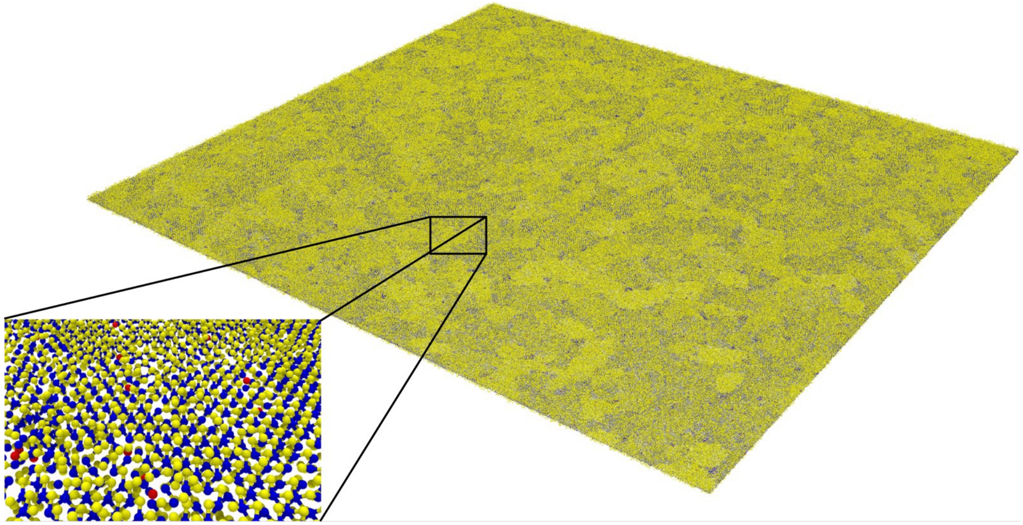
High-temperature sulfurdization of MoO_3 monolayer with S_2 gas

Step 1. O_2 evolution from a MoO_3 surface

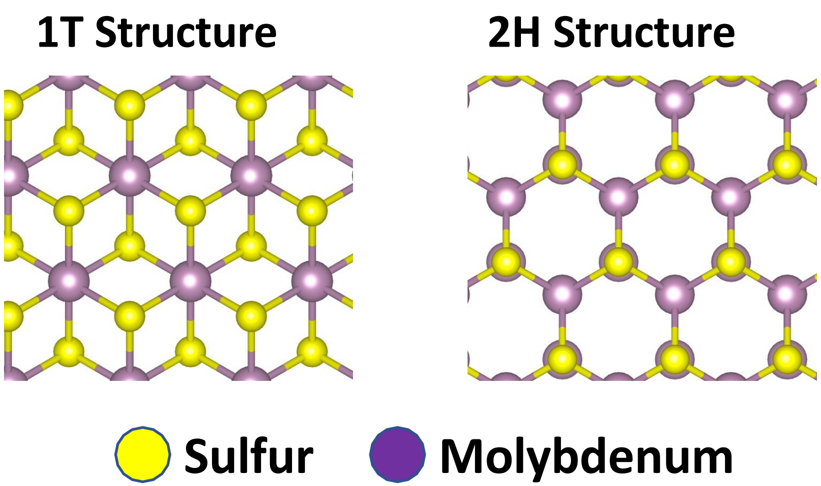
Step 2. SO/SO_2 formation from a $MoO_{2.6}$ surface

Step 3. Mo-S bond formation on MoO_xS_y

MoS_2 Crystal Growth Simulation

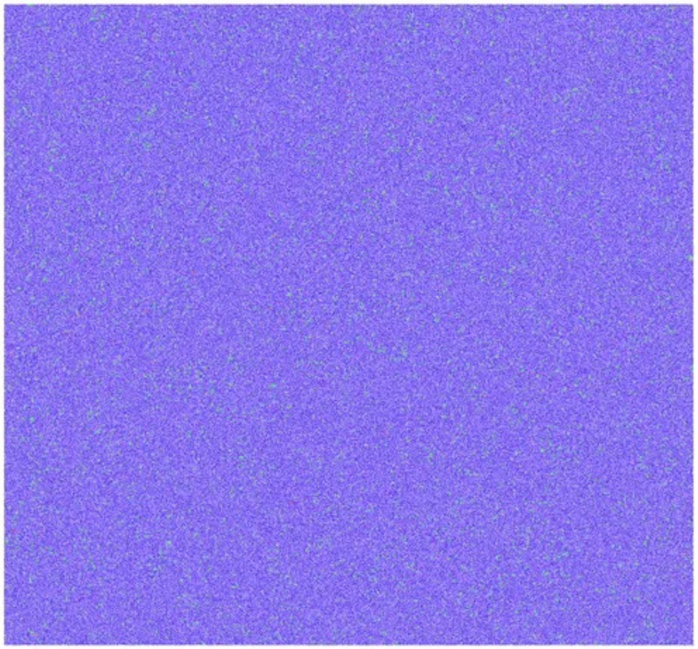


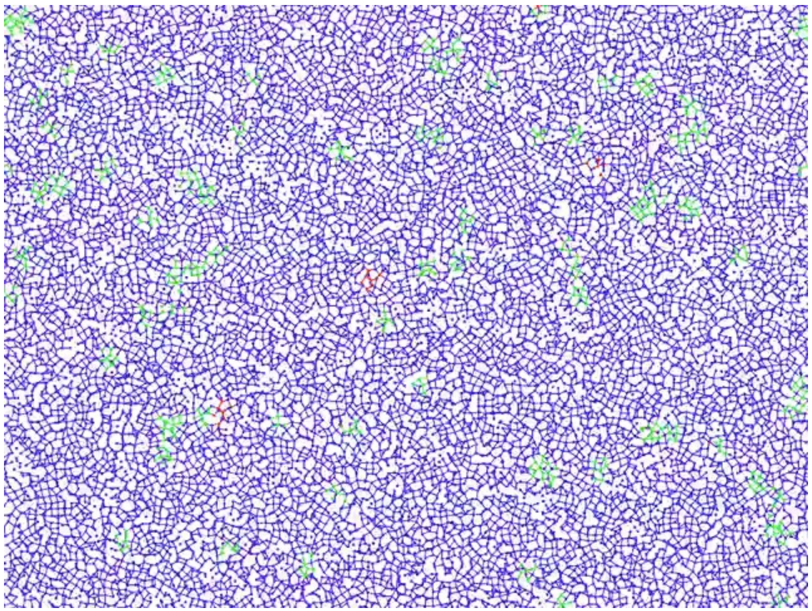
- **Number of atoms:** 4,305,600 atoms (1,497,600 O; 2,347,200 S and 460,800 Mo)
- **System dimensions:** 211.0 × 196.3 × 14.5 (nm^3)
- **Timestep:** 0.75 fs.



The pre-sulfurized MoS slab is thermalized at 3000K for 1 nsec, quenched to 1000K, then subjected to temperature cycle to improve its crystallinity.

Grain Growth by Annealing





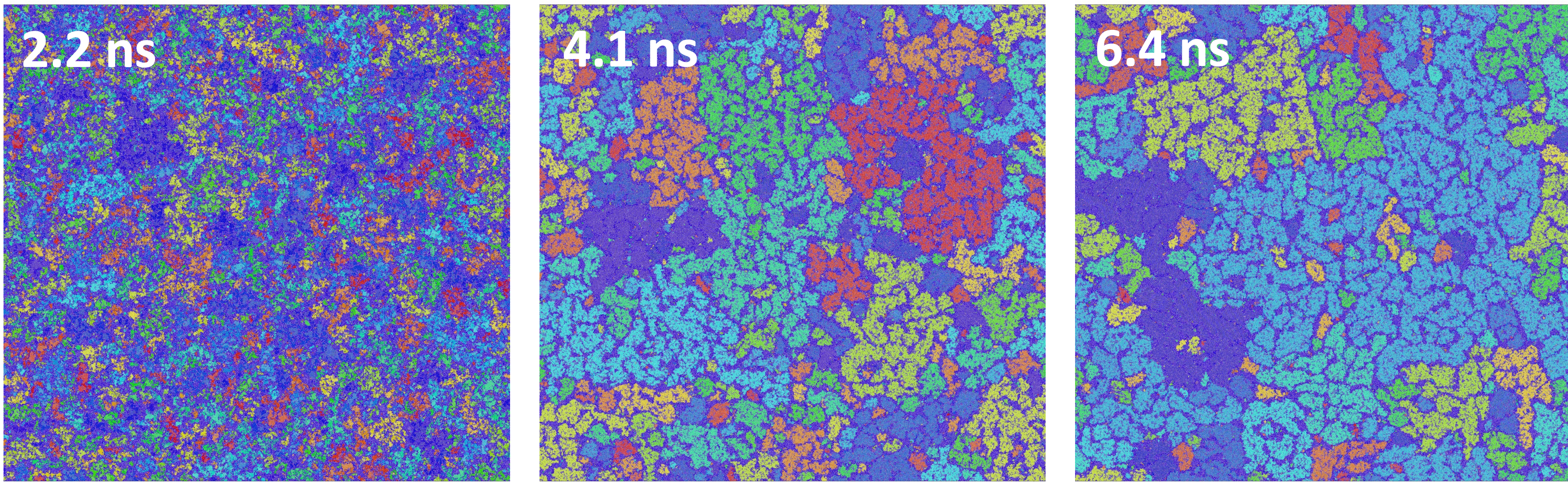
Zoom-in view

1T 2H disordered

- Atoms in the sulfurdized slab are classified into 1T, 2H and disordered phases.
- Areas of connected 2H phase atoms indicates MoS_2 crystal grains, separated by 1T or disordered phases.

Grain Growth by Annealing

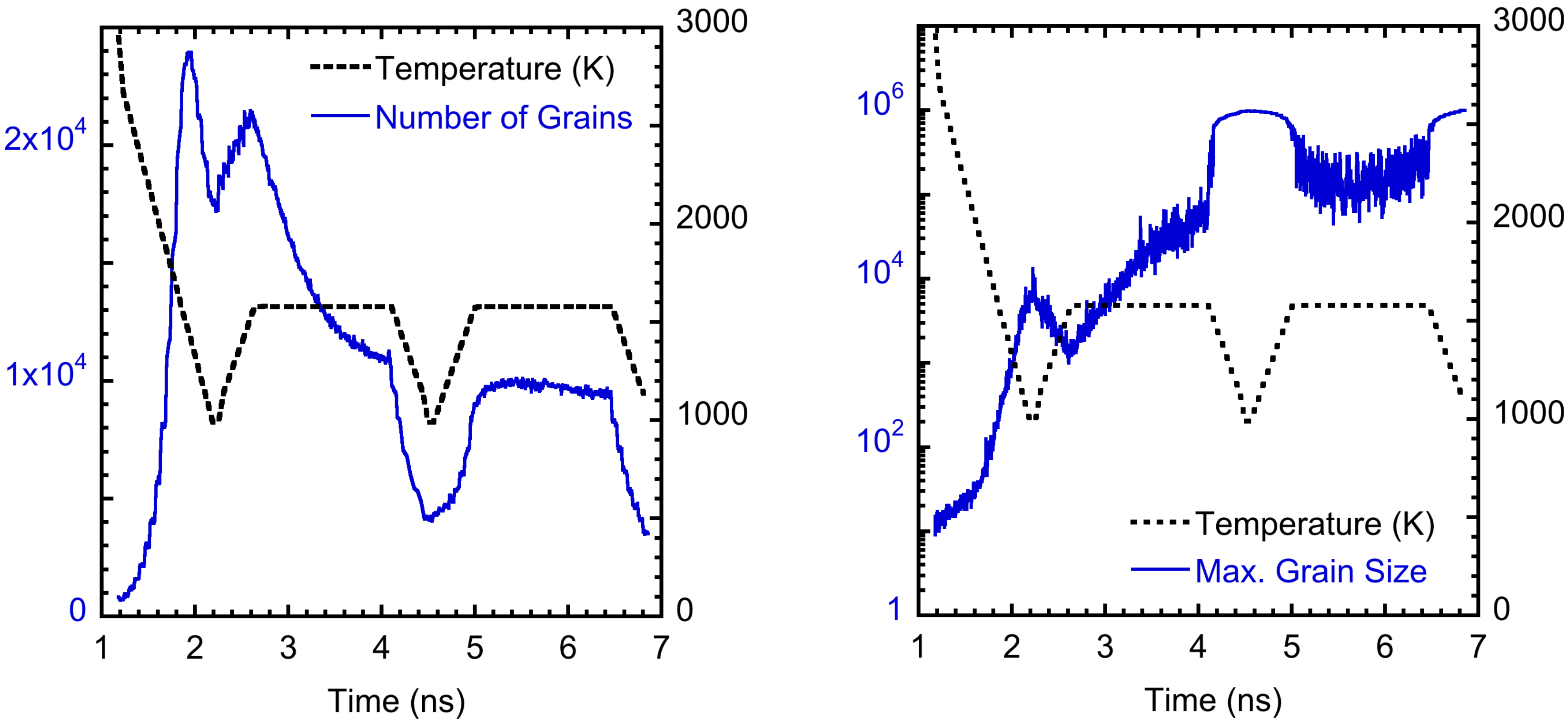
After 1st quench — 1st annealing — 2nd annealing



Color-coded by grain IDs

- **Highly disordered structure is obtained by the rapid quenching at 2.2ns.**
- **Grain growth and crystallinity improvement at 6.4 ns due to the active grain boundary migration.**

Grain Growth by Annealing



- **Rapid decrease in the number of grains and increase in the size of grain during the 1st annealing.**
- **The largest grain continues to grow with a lower rate during the 2nd annealing step.**

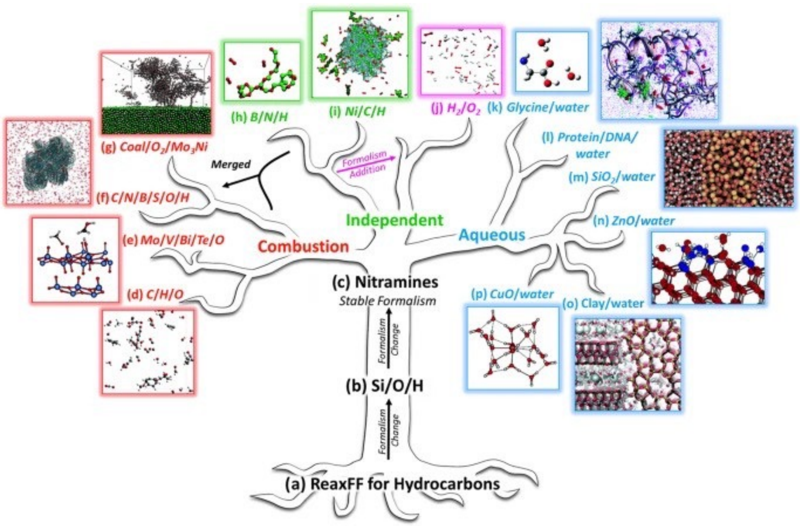
S. Hong, et al. *JPCL* **10**, 2739-2744 (2019)

Moving Forward

Review: The ReaxFF reactive force-field: development, applications and future directions*
https://www.nature.com/articles/npjcompumats201511

List of published ReaxFF force fields
https://www.scm.com/doc/ReaxFF/Included_Forcefields.html

Interatomic potential repository
https://www.ctcms.nist.gov/potentials/



ReaxFF development tree*

Recent advances in RMD:

- eReaxFF: A Pseudoclassical Treatment of Explicit Electrons within Reactive Force Field Simulations https://pubs.acs.org/doi/10.1021/acs.jctc.6b00432
- JAX-ReaxFF: A Gradient Based Framework for Extremely Fast Optimization of Reactive Force Fields https://chemrxiv.org/engage/chemrxiv/article-details/60e0d9496b8d89786e6b8a06
- Machine learning potentials for extended systems: a perspective https://link.springer.com/article/10.1140/epjb/s10051-021-00156-1